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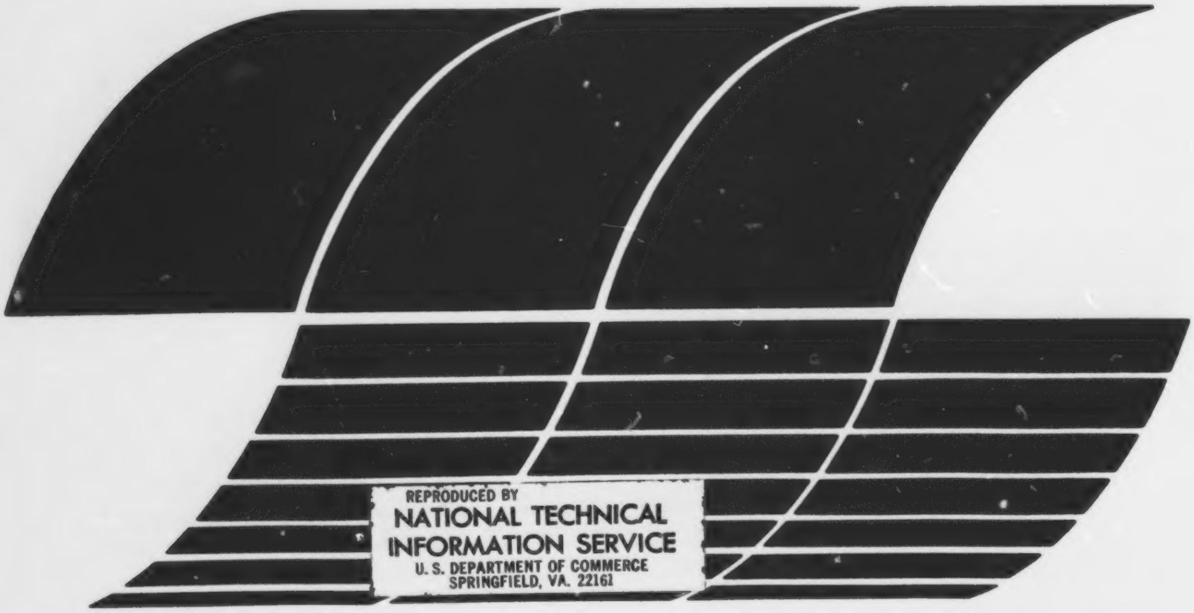

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The report gives results of an evaluation of the applicability of refinery control technologies to coal conversion. It is part of a comprehensive program for the environmental assessment of high-Btu gasification technology. Process/waste streams from coal gasification and liquefaction processes were characterized. Streams with refinery counterparts were identified. Toxicological and health effects data were also collected on waste stream constituents. Control technologies used in refineries to manage the identified streams were evaluated and their applicability to counterpart coal conversion streams was assessed. Study results indicate that, despite similarities between the refinery process/waste streams and their coal conversion counterparts, significant composition differences between the analogous streams would affect applicability and design of a control technology. Many refinery processes, which appear to have applicability to coal conversion process/waste streams, have not been tested for such applications. Additional testing would be necessary to generate data needed for a more accurate determination of their applicability.

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ABSTRACT

This report has been prepared as part of a comprehensive program for the environmental assessment of high Btu gasification technology. The program is being directed by the Fuel Process Branch of EPA's Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina.

Due to certain gross similarities which exist between refinery and coal conversion waste streams and the considerable experience which exists in refinery pollution control, the evaluation of the applicability of refinery control technologies to coal conversion is a logical step in the assessment of coal conversion control technology needs. Lurgi, Koppers-Totzek and COED processes were examined as example processes for high-Btu, low/medium-Btu and liquefaction coal conversion processes, respectively. The process/waste streams from these processes were characterized and those streams having refinery counterparts were identified. As part of the program, toxicological and health effects data on select waste stream constituents were also collected. The control technologies currently used in refineries for the management of the identified streams were evaluated and their applicability to counterpart coal conversion streams was assessed.

The results of the study indicate that, despite a number of similarities between the refinery process/waste streams and their coal conversion counterparts, there are significant composition differences between the analogous streams which would affect applicability and design of a control technology. Many of the refinery processes which appear to have applicability to coal conversion process/waste streams have not been tested in such applications and additional testing would be necessary to generate data needed for a more accurate determination of their applicability.

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1.0 INTRODUCTION

Recognizing the dwindling domestic supplies of natural gas and crude oil and the importance of reducing the country's current dependence on foreign sources of energy, government and private industry are currently expending considerable effort to develop alternate sources of domestic fuel. Because of the abundance of mineable coal reserves in the U.S., the greater use of coal, directly or after conversion to substitute natural gas or oil products, is one of the alternatives receiving serious consideration. Development of a viable synthetic fuel industry must be accompanied by efforts to anticipate environmental problems, identify control technology needs, and develop appropriate controls and bases for establishing regulations.

In response to the shift in the U.S. energy supply priorities from natural gas and oil to coal, the Environmental Protection Agency has initiated a comprehensive assessment program to evaluate the environmental impacts of synthetic fuels from coal processes having a high potential for eventual commercial application. This overall assessment program is being directed by the Fuel Process Branch of EPA's Industrial Environmental Research Laboratory, Research Triangle Park (IERL-RTP). The primary objectives of the EPA synthetic fuels from coal program are to define the environmental effects of synthetic fuel technologies with repsect to their multimedia discharge streams and their health and environmental impacts and to define control technology needs for an environmentally sound synthetic fuel industry. The synthetic fuel technologies being addressed in the EPA program include high Btu gasification, low/medium Btu gasification and coal liquefaction. Under a contract with EPA, TRW is currently conducting an environmental assessment of high Btu gasification technology. One element of this program involves the evaluation of the applicability of petroleum refining control technologies to the production of synthetic fuels from coal.

The potential for the application of refinery controls to synthetic fuel production stems from certain gross similarities which exist between the waste streams in the two industries. Petroleum refining is a well-established industry. Many types of pollution control equipment and systems are in use in refineries and the industry has been very active in developing new environmental control technologies and improving the existing ones to minimize discharges and to meet environmental regulations. The objective of this program has been to identify and review those refinery control technologies which would have application to coal conversion process/waste streams. The effort has consisted primarily of a review of the available data to (a) determine and characterize refinery process/waste streams which have counterparts in coal conversion facilities; (b) review control technologies which have been applied to the identified refinery waste streams and other refinery control technologies which may be applicable to coal conversion streams not having counterparts in petroleum refining; and (c) evaluate the applicability and adaptability of the refinery control technologies to coal conversion. In addition, data were collected on toxicological and health effects of potentially hazardous components in analogous refining and coal conversion waste streams.

The data used for process/waste stream characterization and for control technology evaluation were obtained from several sources including (a) published and unpublished EPA documents, (b) open literature, (c) process developers and EPA/DOE contractors, and (d) authorities in industry and academic institutions. Based on the preliminary review of the collected data, a number of coal conversion and related processes, which were judged to have a greater likelihood of being employed in commercial facilities, were selected and analyzed in more detail. For each coal conversion process and refinery control technology reviewed, a data sheet was prepared presenting key information items and thereby imparting high visibility to engineering "facts and figures," allowing ready comparison between alternate processes, and underlining specific areas where significant gaps existed in the available data. To assure the completeness and accuracy of the information, where applicable, the data sheets on the processes reviewed were forwarded to the process developers/licensors for review and comment. A complete set of the data sheets prepared has been incorporated as Appendices to a separate document entitled "Environmental Assessment Data Base for High-Btu Gasification Technology," prepared for EPA under the current contract. The sources used in the preparation of the data sheets have been identified in each sheet. In this report the references to the sources of data which were extracted directly from the data sheets have not been repeated.

2.0 SUMMARY AND CONCLUSIONS

As a first step in the determination of the applicability of the refinery control systems to coal conversion waste streams, the refinery waste streams were reviewed and those likely to have counterparts in coal conversion were characterized. Based on the considerations of (a) availability of data on waste stream characteristics, (b) attainment of or nearness to commercial status, (c) representation of integrated operations producing upgraded or refined gaseous or liquid products, and (d) avoidance of duplicity in related EPA programs, three coal conversion processes were selected as examples of high-Btu gasification, low/medium-Btu gasification and liquefaction technologies. These processes are Lurgi, Koppers-Totzek and COED. The process/waste streams from these processes were characterized and those streams having refinery counterparts were identified. The refinery control technologies were then evaluated from the standpoint of applicability to counterpart waste streams in coal conversion.

Compared to the relatively large amount of actual data available for many refinery waste streams, very few data are available for waste streams generated in integrated commercial coal conversion plants. The insufficiency of characterization data on coal conversion waste streams, which constitutes a major obstacle to accurate and detailed assessment of the applicability of refinery control technologies to coal conversion waste streams, stems primarily from the nonexistence of commercial SNG and liquefaction facilities in the U.S. and from the nonapplicability of some of the data from U.S. pilot coal conversion facilities to large-scale operations. For many of the unit operations where some discharge stream characterization data are available, such data are not comprehensive in that not all streams are addressed and not all potential pollutants and toxicological and ecological properties are defined. Commercial gasification and liquefaction facilities in operation in foreign countries do not generally incorporate design and operating features which would likely be employed in a facility in the U.S. to minimize waste generation and to control discharge. Moreover, the coals used at these facilities differ from those which will be employed at commercial plants in the U.S. Although many of the unit operations for gas and liquid processing which may have applications in commercial coal conversion have been tested or used commercially in other industries, their performance in coal conversion service has often not been evaluated.

Based on the review of the available data and from a control technology applicability viewpoint, a limited number of refinery and coal conversion process/waste streams appear to have certain similar characteristics. These streams and the basis for their similarities are listed in Table 2-1. Despite the noted similarities, there appears to be significant composition differences between the analogous streams which would affect applicability and design of a control technology. For example, while both the refinery process sour gases and the quenched product gas from coal gasification contain H_2S and CO_2, the H_2S concentration is considerably higher and the CO_2 level is significantly lower in most refinery sour gases (16%-65% vs. 1%-2% and 2%-5% vs. 7%-32%, respectively). Even when selective H_2S removal processes are used, the treatment of the coal conversion raw product gas results in the production of a concentrated acid gas stream with CO_2 levels much higher than those in refinery sour gases. Unlike sour waters from refineries which contain high levels of both sulfides and ammonia, most coal conversion condensates contain low levels of sulfide and moderate levels of ammonia. Because of the differences in the nature of the raw material (crude oil vs. coal) and the processing steps employed, the dissolved and particulate organics (oils, tars, organic acids, etc.) found in coal conversion wastes are different than those in refinery wastewaters. The organics in coal conversion wastes are generally more aromatic while those in refineries are largely aliphatic. These differences in wastewater characteristics also are reflected in the characteristics of oily sludges and biosludges resulting from wastewater treatment. In comparing coal conversion waste streams with their analogues in refineries, it should be noted that there can be wide differences between stream compositions from different coal conversion plants depending on the coal processed, conversion process used and on-site product upgrading methods employed.

TABLE 2-1. SIMILAR REFINERY AND COAL CONVERSION WASTE STREAMS

Refinery Streams	Coal Conversion Counterparts	Major Similarities
Gaseous		
Process sour gas	Quenched product gas, acid gas and fuel gas (from liquefaction)	High H_2S and ammonia content; presence of CO_2
Catalyst regenerator off-gas	Raw product gas and char combustion flue gas	High CO and particulates, NO_x and N_2
Fugitive emissions	Fugitive emissions	Hydrocarbons, sulfur compounds, ammonia
Liquid		
Sour waters	Raw product gas quench condensate waste liquor purge (from liquefaction) and shift condensate	Ammonia, sulfide, phenols, oils and grease/tars
Oily waters	Raw product gas quench condensate and waste liquor purge (from liquefaction	Oil and grease/tar; phenols
Solid		
Spent catalysts	Spent shift, methanation, hydrotreating, and Claus plant catalysts	Metals (Ni, Co, Mo, etc.), bauxite
Sludges	Oily and biosludges	Oil and grease/tar, inerts, biomass, refractory organics

The refinery control technologies which may find application to coal conversion are listed in Table 2-2. Some of the control processes (e.g., sulfur recovery plant tail gas treatment processes) would be applicable to waste streams in a coal conversion plant and their design may be essentially the same as in refinery applications. Other processes such as Stretford, Claus and steam stripping would require extensive modifications to account for differences in waste compositions. Because of limited data on certain waste characteristics (e.g., biodegradability of organics and settleability of suspended solids in wastewaters), the applicability and efficiencies of processes such as bio-oxidation, flotation, sludge dewatering, and emulsion breaking in coal conversion application cannot be accurately assessed at this time. With the exception of very few processes which have been tested in coal conversion applications (e.g., Rectisol and DGA acid gas treatment processes and Stretford tail gas treatment process), the processes listed in Table 2-2 have not been employed in such an application. For the processes which have been used in coal conversion, only limited data are available on process design and performance. Even though the processes listed in Table 2-2 appear applicable to coal conversion wastes, the true test of applicability and definition of criteria for large-scale design and cost estimation require additional testing. It should also be noted that the suitability of a control process for use in coal conversion plants cannot be determined separately from other processes and waste treatment operations within an integrated coal conversion facility. The selection of a specific control process is merely an element in the overall waste management plan for a facility which includes considerations of overall emissions/effluent limitations, energy and raw material availability and costs.

Some of the components in refinery and coal conversion wastes are important from the standpoint of presenting potential occupational health hazards to plant workers and adverse health impact on the general population. Several of the hazardous waste components, i.e., H_2S, CO and mercaptans, are not unique to refinery or coal conversion wastes and are emitted from a variety of other industrial and nonindustrial sources. The hazardous characteristics of many of these commonplace substances are generally well documented. The hazardous chemicals which are unique to coal conversion and refineries fall into three categories: polynuclear aromatics, heavy metals and organometallic

TABLE 2-2. REFINERY CONTROL TECHNOLOGIES AND THEIR APPLICABILITY TO COAL CONVERSION

Refinery Control Technology	Applicability to Coal Conversion Waste Stream
Acid Gas Treatment	
Amine Solvents (DEA, Fluor Econamine, ADIP, etc.)	Potentially suitable for non-selective removal of H_2S and CO_2 from product gases from atmospheric/low pressure gasification/liquefaction. Also suitable for hydrocarbon removal from concentrated acid gases and for concentrating dilute H_2S streams for feeding to Claus plant. Extensive solvent degradation may be encountered in coal application.
Physical Solvents (Selexol, Rectisol, etc.)	Potentially suitable for selective removal of H_2S and CO_2 from product gases. Best suited to high pressure application. The resulting concentrated acid gas stream may contain high levels of hydrocarbons, thus requiring further treatment prior to sulfur recovery.
Sulfur Recovery	
Claus	Split-flow mode applicable to coal conversion acid gases containing more than 10% H_2S. Sulfur burning mode applicable to feeds containing as low as 5% H_2S. Removal of ammonia and hydrocarbons from feed gases would be required to prevent ammonium bicarbonate scaling and carbon deposition on catalyst, respectively.
Stretford	Most existing applications are to acid gases containing low levels (around 1%) of H_2S. High CO_2 levels necessitate pH adjustment and result in high blowdown rates. Relatively large unit sizes would be required with high CO_2 gases. Process does not remove non-H_2S sulfur compounds.
Tail Gas Treatment	
IFP-1, Sulfreen	Suitable for Claus plant tail gas treatment; cannot achieve very low levels of total sulfur in the off-gas which may be required by emission regulations. Efficiency decreases with increasing CO_2 level in the feed.
SCOT, Beavon and Cleanair	Sulfur removal efficiencies decrease and CO_2 levels in tail gas increase when acid gases contain high CO_2 levels

(continued)

TABLE 2-2. CONTINUED

Refinery Control Technology	Applicability to Coal Conversion Waste Stream
Tail Gas Treatment (contd)	
Chiyoda Thoroughbred 101, Wellman-Lord, IFP-2 and Shell CuO	Potentially suitable. Requires feed incineration to convert reduced sulfur to SO_2.
Fugitive Emissions and Odor Control	
Vapor recovery, incineration, source elimination	Applicable to analogous sources.
Sour Water Stripping	
Conventional Stripping and Chevron WWT Process	Applicable to coal conversion sour waters. The design must be modified to allow for the lower sulfide and often higher ammonia levels in coal conversion sour waters.
Oily Water Treatment	
API Separator and Flotation	Applicable; units must be designed based on specific wastewater characteristics.
Biological Wastewater Treatment	Generally applicable; biodegradability of coal conversion waste components not established.
Carbon Adsorption and Chemical Oxidation	Should be applicable; design basis must be established for the specific wastewater.
Slop Oils and Sludge Treatment (thickening, centrifugation, emulsion breaking, drying beds)	Generally applicable; design basis must be established for the specific waste.
In-Plant Waste Volume and Strength Reduction	Applicable.
Resource Recovery	Applicable to spent catalysts for material recovery; sale of tars/oils
Incineration	Applicable to organic wastes, incinerator and emission control designs would be feed specific.
Land Disposal	Applicable.

compounds, and low molecular weight aromatic substances. Many of the control technologies used in both refineries and coal conversion plants should result in partial or total removal of the hazardous waste components. The fate of many of the hazardous components in pollution control processes is not well-known, and the requirements for additional controls cannot be defined at this time.

3.0 RECOMMENDATIONS

- Additional data on the characteristics of waste streams from coal conversion plants are needed and should be obtained from process developers and through sampling and analysis at commercial and pilot plant facilities.
- Very few performance data are available on certain control units which are known to be in operation at a number of specific refineries. Data available on these units should be solicited from the plants. If adequate data are not currently available, a sampling and analysis program should be conducted to generate the needed data.
- A few refinery control technologies have been used in coal conversion and similar applications (e.g., coke and natural gas industries). Engineering and actual performance data on these processes should be obtained from owners/licensors or through plant monitoring.
- The performance of refinery control technologies which appear applicable to coal conversion waste streams should be evaluated through laboratory, bench- and pilot-scale testing using actual or simulated coal conversion wastes. Such testing should generate the necessary data for scale-up and cost estimation and should enable more accurate definition of process capabilities and limitations.
- Because of the reported wide variations in stream compositions among refineries, it is possible that a stream composition in some refineries may be closer to its counterparts in a coal conversion plant than a similar stream in another refinery. Asssitance should be solicited from refineries or their trade association to identify such streams and to obtain performance data on any control technologies applied.

4.0 CHARACTERISTICS OF PETROLEUM REFINERY WASTE STREAMS

Gaseous, liquid and solid discharges from petroleum refining operations are identified and characterized in this chapter. Only the refinery streams which may correlate with those expected from coal conversion processes are characterized. Thus, some significant sources of petroleum refinery emissions may not be detailed in this chapter because similar streams are not likely to be encountered in coal conversion processes.

Rates and characteristics of emissions from petroleum refineries may vary significantly because of differences in the nature of crude oils refined and in the operating conditions and/or processes employed. The waste streams identified and characterized in this chapter generally represent those for a "typical" modern refinery and are based on information published in the literature.

4.1 GASEOUS WASTE STREAMS

Figure 4-1 shows a typical modern refinery with major product and gaseous waste streams. Seven categories of gaseous process/waste streams (numbered 1 through 7), which constitute the major emissions from a refinery, are identified. General descriptions of these streams, including their sources, major contaminants and control technologies currently used (if any), are presented in Table 4-1.

The seven streams listed in Table 4-1 were reviewed from the standpoint of (a) similarity of composition to the process/waste streams in coal conversion facilities, and (b) applicability of the currently used refinery control technologies to a process/waste stream in coal conversion plants. Based on composition similarity considerations, two streams (Stream Nos. 1 and 2) were determined to have possible counterparts in coal conversion. Detailed composition data were collected for these two streams.

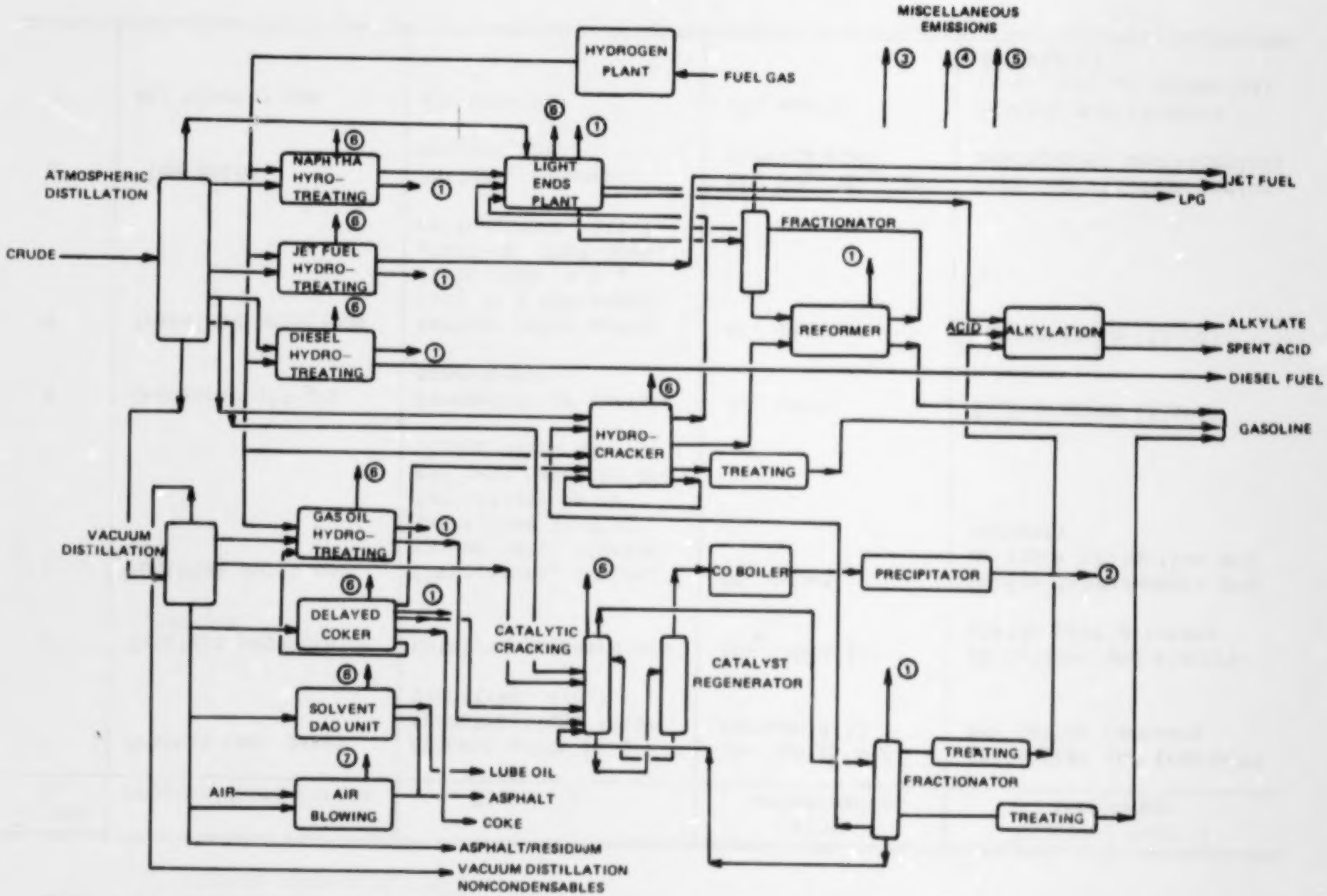
MISCELLANEOUS EMISSIONS
③
④
⑤
HYDROGEN PLANT
FUEL GAS
ATMOSPHERIC DISTILLATION
CRUDE
NAPHTHA HYRO-TREATING
JET FUEL HYDRO-TREATING
DIESEL HYDRO-TREATING
LIGHT ENDS PLANT
FRACTIONATOR
REFORMER
ACID
ALKYLATION
JET FUEL
LPG
ALKYLATE
SPENT ACID
DIESEL FUEL
GASOLINE
HYDRO-CRACKER
TREATING
VACUUM DISTILLATION
GAS OIL HYDRO-TREATING
DELAYED COKER
SOLVENT DAO UNIT
AIR
AIR BLOWING
CATALYTIC CRACKING
CO BOILER
PRECIPITATOR
CATALYST REGENERATOR
FRACTIONATOR
TREATING
TREATING
LUBE OIL
ASPHALT
COKE
ASPHALT/RESIDUUM
VACUUM DISTILLATION NONCONDENSABLES
①
②
⑥
⑦

Figure 4-1. Major Refinery Process and Gaseous Waste Streams(11) (See Table 4-1 for Waste Stream Descriptions)

TABLE 4-1. CHARACTERISTICS OF PERTINENT PROCESS/WASTE GASEOUS STREAMS IN A REFINERY AND APPLICABLE CONTROL TECHNOLOGIES(2)

Stream No.	Process/Waste Stream	Source(s)	Major Contaminants	Existing Control Technology
1	Process sour gases	Process units (e.g., hydrotreating, fractionating, etc.)	See Tables 4-2 through 4-12	Collection and treatment for sulfur recovery
2	Catalyst regenerator off-gas	Catalyst regenerators	See Table 4-6	CO boilers and electrostatic precipitators
3	Fugitive emissions	Compressors, drains, vacuum jets, storage tanks, and loading facilities; waste effluent handling and sludge disposal	HC, odors	Design improvements and/or vapor collection and recovery
4	Condenser off-gas	Barometric or surface condensers	HC, odors	Incineration (flare)
5	Transient emissions	Various units operating in a non-steady state mode (e.g., start-up, shut-down, malfunctions, etc.)	HC, odors	Incineration (flare)
6	Flue gases	Boilers, furnaces, heaters, etc.	HC, SO_x, NO_x, and particulates	Fuel substitution and/or operational modifications
7	Air blowing gas	Air blowing	HC, odors	Process modification (e.g., use of mechanical agitators)

The refinery control technologies used on Streams 3, 4 and 5 (vapor recovery and incineration) were identified to have possible applications in coal conversion plants for hydrocarbon control from vents, storage tanks, etc. The vapor recovery and incineration technologies and the control technologies associated with Streams 1 and 2 and their applicability to coal conversion process/waste streams are evaluated in Section 6.1.

Stream 6 (flue gas) has counterparts in coal conversion, but the refinery control (use of clean fuel and operational modification) would have very limited applicability to coal conversion (see Section 5.2.6). Stream 7, air blowing off-gas, has no counterpart in coal conversion plants.

Brief descriptions of the seven streams listed in Table 4-1 and the rationale for the selection of streams/refinery technologies for technology applicability evaluation follows.

4.1.1 Stream No. 1, Process Sour Gases

Sour gases containing hydrocarbons and sulfur impurities are sent to a sour gas treating unit for sulfur removal (see Section 6.1). The "sweetened" (cleaned) gas can then be used to fire process heaters, furnaces and boilers without requiring flue gas cleaning.

Figure 4-2 presents a schematic diagram of gas treatment and sulfur recovery, identifying the input, intermediate and product streams. The input stream (No. 1) which originates from various refinery process vessels varies considerably in composition. (In a refinery, the gas treating units are often located near the process units and may handle gases from only one or several nearby units.) The input sour gas is generally high in H_2S content (a range of 16% to 62% has been reported, see below) and contains a significant amount of hydrocarbons.

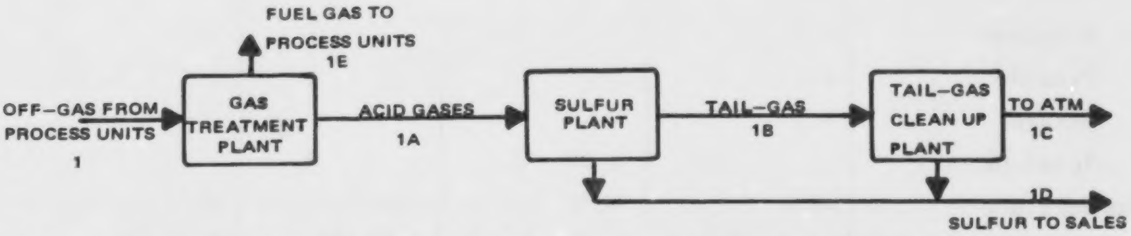

Figure 4-2. Gas Treatment and Sulfur Recovery Processes (stream numbers refer to compositions shown in Tables 4-2 through 4-5)

Several different processes are currently used in refineries for sour gas treatment, sulfur recovery and sulfur plant tail gas treatment (see Section 6.1). The compositions of the intermediate and product streams (Stream 1-A, 1-B, 1-C, 1-D and 1-E in Figure 4-2) from these operations would depend on the nature of the processes employed as well as the composition of the input sour gas. Only limited waste stream data have been reported for a few of the process combinations which are currently in use. These data are summarized in Table 4-2 and are detailed in Tables 4-3, 4-4, and 4-5 for the process combinations identified.

TABLE 4-2. GAS TREATMENT AND SULFUR RECOVERY STREAM COMPOSITIONS(3,4,9,5,6,7)

Parameter	Gas Treatment		Sulfur Plant	Tail Gas
	1	1A	1B	1C
Components, Vol. %				
H_2S	16.4 - 62.5	50.3 - 91.9	0.5 - 1.20	0.0 - 0.03
SO_2			0.25 - 0.60	
S_8 vapor/mist			0.01 - 0.02	
COS			0.03 - 0.05	10 - 250 ppm
CS_2			0.03 - 0.50	0.1 - 1 ppm
CO_2	1.9 - 4.9	4.6 - 46.1	0.04 - 3.5	3.05 - 19
H_2O			26 - 33.9	5.0 - 7.0
N_2			56 - 65	80.8 - 88.9
H_2			1.6 - 2.5	0.96
CO			1.0	
NH_3		0.1		
Methane	8.4			
Ethane	4.36 - 5.2			
Propane	4.6			
Isobutane	2.5			
N-Butane	7.5			
Pentane	3.4			
Hexane	1.0			
Total HC		0.95 - 2.0		
Temperature	48°C	40°C	140°C	40°C
Pressure		0.15 MPa	0.15 MPa	0.10 PMa

TABLE 4-3. SOUR GAS TREATING STREAM COMPOSITIONS, VOL %: MEA-CLAUS SYSTEM(3)

Gas Stream Components/Parameters	Stream Designation*		
	1	1A	1B
H_2S	62.5	91.4	1.07
SO_2	--	--	0.89
CO_2	4.9	8.15	--
H_2O	--	--	--
N_2 + inerts	--	--	--
Methane	8.4	--	3.35
Ethane	5.2	--	32.31
Propane	4.6	--	62.38
Isobutane	2.5	--	--
N-Butane	7.5	--	--
Pentane	3.4	--	--
Hexane	1.0	--	--
HC	--	0.45	--

*See Figure 4-2 for stream definitions

TABLE 4-4. SOUR GAS TREATING STREAM COMPOSITION, VOL % ; 2-STAGE AND 3-STAGE CLAUS(4)

Gas Stream Components/Parameters	2-Stage Claus* 1A‡	2-Stage Claus* 1B	2-Stage Claus† 1A	2-Stage Claus† 1B	3-Stage Claus 1A	3-Stage Claus 1B
H_2S	50.3	0.7	83.5	0.8	90.0	1.0
SO_2	--	0.3	--	0.4	--	0.5
S	--	0.2	--	0.3	--	--
CO_2	46.1	21.8	11.5	4.4	8.0	3.5
H_2O	--	25.5	4.0	33.9	--	30
N_2	1.0	51.5	0.4	60.2	--	65
O_2	--	--	--	--	--	--
Methane	2.5	--	0.5	--	--	--
NH_3	--	--	0.1	--	--	--
HC	--	--	--	--	2	--

*Stauffer Chemical Co., Baytown, Texas refinery

†Stauffer Chemical Co., Long Beach, Ca. refinery

‡1A and 1B refer to streams shown in Figure 4-2.

As discussed in Section 5.2, the counterpart of the refinery sour gas in a coal conversion plant is the quenched product gas which in a commercial facility will be treated for the removal of sour components. The composition of the quenched product gas differs from that of the refinery sour gas (Stream 1, Figure 4-2) primarily with respect to the concentrations of CO_2, H_2S, CO and H_2. The quenched product gas generally contains a considerably smaller concentration of H_2S and significantly higher concentrations of CO_2, H_2 and CO.

4.1.2 Stream No. 2, Catalyst Regenerator Off-Gases

The typical composition range for the fluid catalytic cracking off-gas is presented in Table 4-6. As indicated in this table, the off-gas generally

TABLE 4-5. SOUR GAS TREATING STREAM COMPOSITIONS, VOL % ; CLAUS PLANT WITH SCOT, BEAVON, WELLMAN-LORD, IFP-1, CHIYODA THOROUGHBRED 101 AND SULFREEN TAIL GAS TREATMENT SYSTEMS(4)

Gas Stream Components/Parameters	Gas Treating (type unknown) 1A*	Claus 1B	SCOT 1C	Beavon 1C	Wellman-Lord 1C	IFP-1 1C	Chiyoda Thoroughbred 101 1C	Sulfreen 1C
H_2S	89.9	0.85	0.03	10 ppm	--	0.085	--	0.180
SO_2	--	0.42	--	0.0	250 ppm	0.042	0.10	0.085
S_8 vapor+mist	--	0.05	--	--	--	--	--	--
S	--	--	--	0.0	--	0.050	--	0.013
COS	--	0.05	10 ppm	75 ppm	--	0.050	--	0.051
CS_2	--	0.04	1 ppm	75 ppm	--	0.075	--	0.050
CO	--	--	--	0.29	--	0.219	--	0.222
CO_2	4.6	0.22	3.05	4.49	5.33	2.376	4.928	2.39
HC (MW:30)	--	--	--	0.08	--	--	--	--
H_2	--	1.60	0.96	0.30	--	1.607	--	1.62
H_2O	5.0	33.10	7.00	6.59	8.88	33.990	15.582	33.44
N_2	--	61.30	88.9	88.24	83.98	61.545	77.822	61.93
Ethane	0.5	--	--	--	--	--	--	--
O_2	--	--	--	0.0	1.81	--	1.579	--
Temperature	310°K (104°F)	410°K (284°F)	310°K (104°F)	310°K (104°F)	316°K (110°F)	390°K (247°F)	330°K (130°F)	310°K (284°F)
Pressure	0.15 MPa(21 psia)	0.15 MPa(21 psia)	0.10 MPa(15 psia)	0.1 MPa(15 psia)	0.1 MPa(15 psia)	--	0.1 MPa(15 psia)	0.1 MPa (15 psia)

*1A, 1B and 1C refer to streams shown in Figure 4-2.

contains significant concentrations of particulates and carbon monoxide. In refinery practice the carbon monoxide is converted to carbon dioxide in a "CO boiler" (which also recovers the sensible heat) and the particulates are removed by an electrostatic precipitator prior to the discharge of this stream to the atmosphere.

TABLE 4-6. COMPOSITION RANGE FOR FLUID BED CATALYTIC CRACKING REGENERATOR OFF-GAS*

Constituents	Mole %
SO_2	0.12 - 0.16
SO_3	less than 0.001
Aldehydes	0.001 - 0.005
NO_x	0.01 - 0.035
Organic Acids	0.0005 - 0.002
HC (as Hexane)	0.1 - 0.3
Particulates	0.7 - 35 g/Nm^3 (0.3-15 grains/scf)
CO_2 (dry)	6 - 9
CO (dry)	6 - 7
O_2 (dry)	1 - 3
N_2 (dry)	81 - 87
Moisture	10 - 35
Temperature	873-943°K (100-1250°F)
Pressure	0.13 - 0.37 MPa (5-40 psig)

*The concentrations shown (excluding particulates, CO_2 and CO) are those reported by the Los Angeles Air Quality Management District based on tests of local refineries(10) ; other pollutant concentrations are from Reference 11.

The closest counterparts of the refinery catalytic regenerator off-gas in a coal conversion plant are the raw (quenched) product gas, the vent gases from lockhoppers, and char combustion flue gases in processes such as Cogas. The similarity to these coal conversion gases relates primarily to the presence of CO and high temperature and the particulate content of the gas. Unlike the raw product gas in a coal conversion plant which is generally high in CO_2 and contains reduced sulfur compounds, the regenerator off-gas is relatively low in CO_2 content and contains oxidized sulfur species (mostly SO_2). The refinery control technology (use of electrostatic precipitators) probably would not be applicable to the processing of coal conversion product gas due to the potential for explosion and the fact that the quenching of the raw product gas which immediately follows gasification results in the removal of particulates. Furthermore, electrostatic precipitators are not generally suited to high pressure applications.

As indicated in Table 4-6, the regenerator off-gas contains a high concentration of nitrogen. When nitrogen is used for lockhopper pressurization in a coal conversion plant, the lockhopper vent gas is expected to be similar to the regenerator off-gas since it would contain a relatively high concentration of nitrogen in addition to its high temperature and particulate content. High temperature electrostatic precipitators, which are sometimes used for the treatment of regenerator off-gas(8), may be applicable to the control of lockhopper vent gases.

4.1.3 Stream No. 3, Fugitive Emissions

Fugitive emissions consist primarily of hydrocarbons and odors which are emitted from a variety of sources in a refinery such as pumps, compressors, storage tanks, drains, open piles, wastewater and sludge processing units, etc. Controls employed on this type of emission depend on the source. For example, fugitives from open drains are commonly controlled by covering the drain and providing a liquid seal to reduce emissions. For pumps, the fugitive emission control consists of using mechanical (rather than packed) seals. For storage tanks either floating roof or vapor recovery systems are used depending on the vapor pressure of stored materials(9).

The characteristics and quantities of fugitive emissions vary within a refinery and among different refineries depending on the emission source (pumps, tanks, etc.), properties of the material handled (volatility, viscosity, pressure, temperature, etc.), age of the equipment and maintenance practices. Since some of the equipment and facilities used in refineries will also be employed in coal conversion plants, such plants are expected to have some of the same sources of fugitive emissions as those encountered in refineries. Although the composition of the fugitive emissions from coal conversion plants might be somewhat different that those from refineries (due to the differences in equipment, products handled and operating conditions), some of these same types of controls will be applicable to coal conversion plants (see Chapter 6.0).

4.1.4 Stream No. 4, Condenser Off-Gas

Barometric condensers are used in refineries (along with vacuum jets) to obtain the vacuum required to operate some process equipment. Water is brought into direct contact with the gas. Mainly for water pollution control reasons, the trend in refining practice has been to replace barometric condensers with surface condensers (indirect cooling); surface condensers are also used in all new U.S. refineries. Unless controlled, the lighter hydrocarbons that are not condensed are released to the atmosphere. Incineration is generally used for the control of these hydrocarbons(2).

The off-gas from barometric or surface condensers does not have a counterpart in coal conversion plants. The incineration control technology which is employed in refineries for the management of the off-gas, however, may have applications in coal conversion.

4.1.5 Stream No. 5, Transient Emissions

Transient emissions are generally associated with start-up and shutdown of equipment and with equipment failures and emergencies. The characteristics of these emissions would vary with the specific type of transient condition and the type of operation/equipment involved. Transient emissions can be minimized by preventive maintenance, proper design for their control and use of appropriate operating procedures. In current refinery practice, transient emissions are controlled by the use of flares. The use of flares for emission control is briefly reviewed in Section 6.1.4.

4.1.6 Stream No. 6, Flue Gases

In refineries, flue gases are emitted from furnaces, boilers and heaters contained in process units or used in steam plants. Because of the process requirements, many of the refining units employ individual, direct-fired, heaters. Accordingly, depending on the size of the refinery, the type of operation employed, and the number of units involved, a large number of relatively small sources of flue gas emissions may exist in a refinery. The quantity and nature of pollutants from each source depend on the type of fuel used and the operating conditions. The types of fuel most commonly used in refineries are internal products, by-products and waste products (e.g., offgases from sour gas treatment, oily wastes, product oil) and natural gas. In the United States, refinery practice for the control of flue gas emissions has been to use clean fuels and/or modify combustion conditions (e.g., use of excess air, burner modification, etc.).

The flue gases encountered in a coal conversion plant and the general nature of the problem and control requirements differ from those for refineries primarily in two respects. First, the types of fuel used in coal conversion plants will be significantly different than those employed in refineries. The probable fuel types in a coal conversion plant will include coal, conversion products (e.g., high and low Btu gas, liquified product) and waste and by-products (e.g., char and coal fines). Second, in a coal conversion plant a centralized utility plant will probably be used to generate steam and/or electric power for the entire complex, in which case the flue gas control technology would be that which has been developed for and used in the utility industry. Accordingly, the flue gas characterization and review of applicable control technology have been eliminated from further consideration in this report.

4.1.7 Stream No. 7, Air Blowing Gas

Air blowing is used in some refineries for "brightening" and agitation of petroleum products or oxidation of asphalt(2). Venting of air used for air blowing results in the emission of entrained hydrocarbon vapors and mists, and malodorous compounds. This type of operation would have no counterpart in a coal conversion facility.

4.2 LIQUID WASTE STREAMS

Figure 4-3 shows liquid waste streams from a typical petroleum refinery. Nearly all refinery designs incorporate a wastewater segregation scheme whereby the process waste streams, which are contaminated with oils, are directed to an "oily waters" sewer and the nonoily process and nonprocess waters are diverted to the "clean waters" sewer. To permit material recovery and pollution control at the "source," the oily process waste streams are further segregated (e.g., sour waters and spent caustics) and treated individually.

Based on the flow diagram shown in Figure 4-3, five major waste streams are identified for a typical refining operation. The general descriptions of these streams (designated Stream Numbers 1 through 5) including their source(s). major contaminants and control technologies currently employed on these streams are presented in Table 4-7. The five liquid waste categories have been reviewed from the standpoint of (a) similarity of major contaminants to the waste streams found in coal conversion facilities and (b) applicability of the currently used refinery control technologies to waste streams from coal conversion plants. Based upon criteria (a) and (b), Streams 1 (sour waters), 3 (the combined plant oily waters to API separator), 4 (clean waters), and 5 (slop oil) have been determined to have counterparts in coal conversion facilities. Stream 2 (spent caustic) has no counterpart in coal conversion plants.

Brief descriptions of the streams listed in Table 4-7 and the rationale for the selection of streams and/or technologies for evaluation of applicability to coal conversion facilities follows. The technologies themselves are evaluated and their applicabilities to coal conversion are discussed in Section 6.2.

4.2.1 Stream No. 1, Sour Waters

Process steam is used in refineries for a range of applications including fractionation and separation of oil products, catalyst regeneration and removal of impurities from products/by-products. Subsequent condensation of steam which has come into contact with products/by-products results in the production of a wastewater which in many cases is characterized by relatively high concentrations of sulfides, ammonia, mercaptans, phenolics and small amounts of organic acids, nitrogen bases and cyanides (see Table 4-8). These waters are referred to as "sour" or "foul" waters. Principal sources of sour

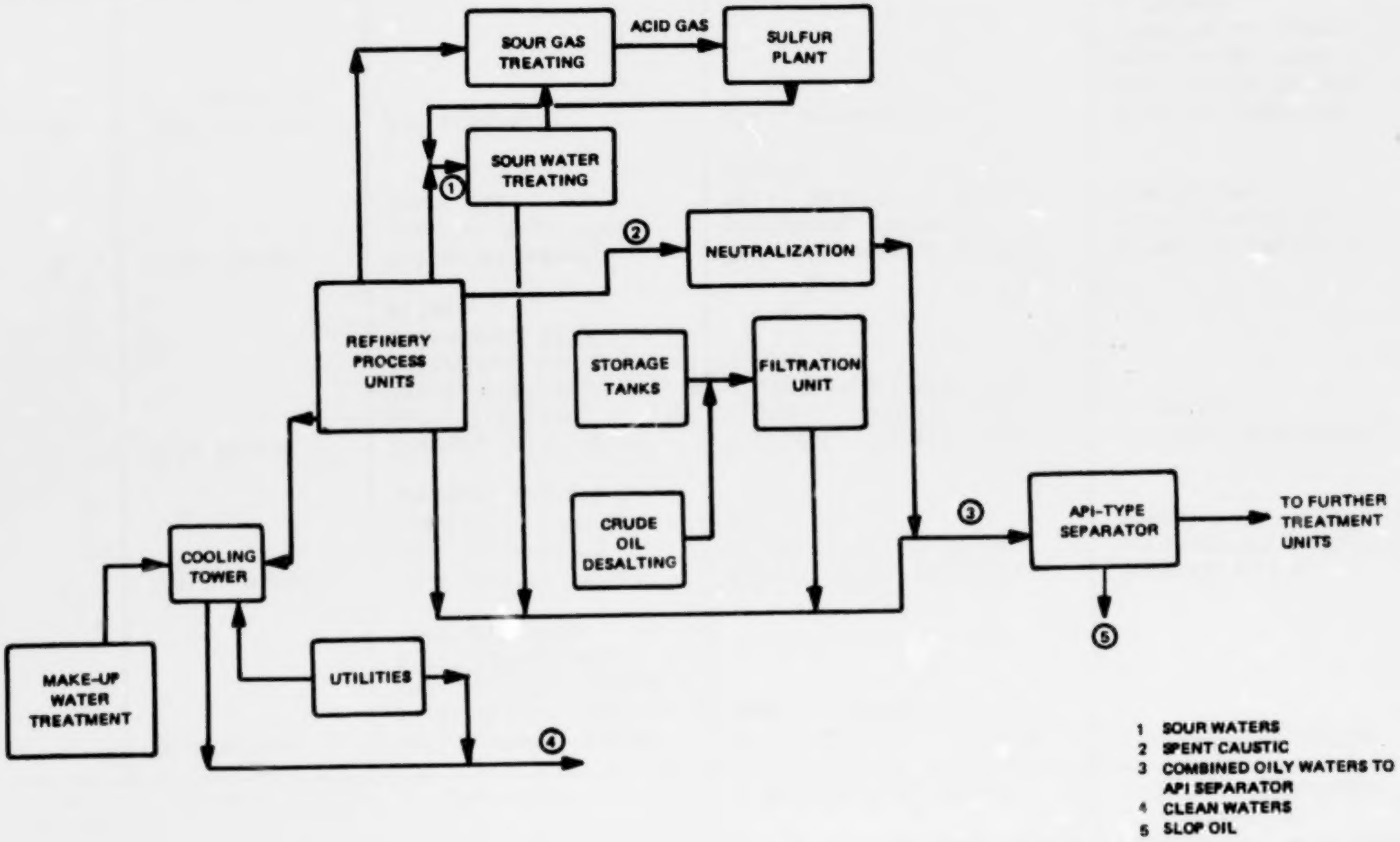
SOUR GAS TREATING
ACID GAS
SULFUR PLANT
SOUR WATER TREATING
①
②
NEUTRALIZATION
REFINERY PROCESS UNITS
STORAGE TANKS
FILTRATION UNIT
CRUDE OIL DESALTING
③
API-TYPE SEPARATOR
TO FURTHER TREATMENT UNITS
⑤
COOLING TOWER
MAKE-UP WATER TREATMENT
UTILITIES
④
1 SOUR WATERS
2 SPENT CAUSTIC
3 COMBINED OILY WATERS TO API SEPARATOR
4 CLEAN WATERS
5 SLOP OIL

Figure 4-3. Refinery Liquid Waste Streams

TABLE 4-7. REFINERY LIQUID WASTE STREAMS(12,13)

Stream No.	Stream	Source(s)	Major Contaminants	Existing Control Technology
1	Sour Waters	Reflux drums, (crude distillation, coking, and cracking) vacuum distillation overhead drum, etc.	Oils, sulfides, phenols, ammonia, acids	Stripping,oxidation
2	Spent Caustic	From caustic scrubs used in removing impurities from petroleum products	Alkali, oils, phenols, organic acid, sulfides, TDS	Neutralization, recovery of crude phenol
3	Oily Waters	Process units, sour water treating, neutralization, filtration and miscellaneous oily waters	Sulfides, phenols, mercaptans, ammonia, and miscellaneous oils and solvents	API-type separators, flotation
4	Clean Waters	Boiler blowdown, cooling tower blowdown, etc.	Moderate amounts of TSS, phosphate, sulfate, small amounts of heavy metals	Direct discharge or maybe treated for process use
5	Slop Oil from API Separator	API separator	Oils, phenols	Emulsion breaking and recycle to process, water from breaking to water treatment

waters are condensates from accumulators, reflux drums and knockout pots in catalytic reformers, cracking, hydrocracking, coking and crude distillation units(12).

TABLE 4-8. REFINERY SOUR WATER CHARACTERISTICS(14,15)

	Typical Value	Range
pH	8.6	7.5 - 9.0
Specific Resistance, ohm-cm	440	-
Alkalinity, ppm as $CaCO_3$	1180	-
Total Dissolved Solids, ppm as $CaCO_3$	1310	-
H_2S, ppm as S	1150	32 - 17,000
NH_3, ppm as N	390	5 - 19,000
Phenolics, ppm as phenol	365	75 - 2400
CN, ppm	4	nil - 28
Suspended Solids, ppm	<8	-
Temperature, °K (°F)	308 (95)	-

In refineries, sour waters are generally treated (by stripping or oxidation) for the removal of the bulk of the contaminants (sulfides, phenols and ammonia) before they are discharged into the plant "oily waters" sewer for additional treatment.

In coal conversion facilities, sour waters result primarily from the quenching of product gas. The characteristics of these sour waters are dependent on the properties of the raw product gas and the quench system employed. The characteristics of these sour waters are presented and compared with those for refinery sour waters, in Section 5.3.

4.2.2 Stream No. 2, Spent Caustic

Typical uses of caustic chemicals in refineries are to neutralize and extract acidic materials that occur in crude oil or in crude fractions, acidic reaction products and acid materials formed during catalytic or thermal cracking (e.g., H_2S, phenolics and acids used as process chemicals/catalysts).

Spent caustic solutions, therefore, may contain sulfides, mercaptans, sulfates, sulfonates, phenolates, naphthenates and other similar organic and inorganic compounds.

Spent caustic is usually treated by neutralization to recover phenols ("acid oils") prior to discharge into the oily waters sewer. In some refineries (usually the smaller ones) the spent caustic is sold to larger reclaimers.

A spent caustic stream similar to the refinery spent caustic waste is not anticipated in a coal conversion facility. Accordingly, the characterization and management of spent caustic wastes have been eliminated from further consideration in this report.

4.2.3 Stream No. 3, Oily Waters

Sources of oily waters are various process units (desalters, barometric condensers, etc.), sour water stripper bottoms, water from treated spent caustics and tank drawoff waters. These waters, which are generally characterized by their content of oils, sulfides, ammonia, and oxygen consuming organics (BOD/COD), are discharged into the oily waters sewer and treated subsequently as a single waste stream. Table 4-9 presents data on the characteristics of the oily wastewater from refineries. Because of the composite nature of the waste and the differences in the processing units employed, types of crude oils handled, and refinery waste management practices employed in different refineries, there are significant variations in the reported composition of the oily wastewaters from different refineries. The composition is also subject to hourly, daily and seasonal fluctuations due to changes in operations (resulting from changes in product mix), the type of crude oil handled, the batch nature of some of the operation steps and the weather conditions (occurrence of rain, etc.).

The closest counterparts of the refinery oily waters in a coal conversion plant are the quench waters from quenching of raw product gases, condensates formed as a result of gas cooling and oily waters from scrubbing of oil products (in coal liquefaction). The composition of the oily waters in a coal conversion plant would differ from that for refinery oily waters. The sources of oily waters in coal conversion plants would be fewer in number and less varied, and these waters are expected to be more uniform in composition.

TABLE 4-9. REFINERY OILY WATER CHARACTERISTICS(16,17)

Parameter	Range (mg/1)	Average Value (mg/1)
Oil	100 - 2600	975
NH_3	160 - 6550	1930
Sulfide (as H_2S)	Trace - 8250	3550
Phenols	10 - 1000	200
BOD	230 - 1000	540
COD	250 - 9600	3100
TOC	32 - 119	75
TSS	6 - 28	20
Alkalinity	80 - 560	320
Ca^{++}	0.3 - 13	5
Mg^{++}	0.5 - 14	3.6
SiO_2	1.3 - 4.4	2
Cl^-	1.5 - 260	82
$SO_4^=$	16 - 125	60
Total $PO_4^=$	0.5 - 3	2
NO_2^-	0 - 276	176
NO_3^-	---	<1
Cu^{++}	0.2 - 0.12	0.06
$Fe^{+2\ \&\ +3}$	0.6 - 1.6	0.9
Zn^{++}	---	0.0
Conductance	250 - 1200 μmhos	560 μmhos
pH	6.8 - 9.6	8.2
Temperature	290-320°K (68-122°F)	308°K (95°F)

Furthermore, because of the differences in the nature of the raw materials (coal vs. crude oils), the coal conversion oily waters contain a significantly higher concentration of tars than refinery oily waters. There will also be some differences in the chemical composition of oils found in the two waste streams. Coal-derived oils tend to be highly aromatic in nature while petroleum oils are primarily paraffinic.

In oil refineries, the common treatment sequence for the processing of oily waters consists of gravity separation (in API type separators), flotation and biological treatment. These control methods and their applicability to coal conversion oily waters are discussed in Section 6.2.

4.2.4 Stream No. 4, Clean Waters

Clean waters are considered to be those that have not contacted oil and are not subject to other contamination for which treatment must be provided. Examples of sources of clean waters include blowdown from cooling towers and boiler, once through cooling waters from surface condensers, etc.

Since these waters contain very little oil, they are usually disposed of directly or reused (e.g., use of boiler blowdown for cooling water make-up), without treatment. In modern refinery practice, however, a small separator or surge pond is used to remove any accidentally introduced oils from these waters before discharge(12). Minimizing the contamination of the clean waters with oils, process chemicals and other wastes is part of a good housekeeping practice at refineries (see Section 6.2.7). Refinery "clean waters" would have counterparts in coal conversion plants and similar control technologies would be applicable.

4.2.5 Stream No. 5, Slop Oil

Slop oils from API-type separators contain oils and oil soluble materials (e.g., phenols). In refineries this stream is generally concentrated by emulsion breaking; the concentrated oil is recycled to the refining operation and the separated water is sent to the biological waste treatment facility.

The counterpart of the refinery slop oil in a coal conversion plant would be the product or by-product oils/tars separated from quench waters or condensates. In most coal conversion facilities the separated oil/tar stream would be further refined (e.g., in hydrotreating of the COED oil), recycled to the gasifier (e.g., in the Lurgi process), combusted on-site for heat recovery or sold. Since for most coal conversion systems the slop oil would be a product or by-product stream and not a waste stream per se, this stream has not been considered for further evaluation.

4.3 SOLID WASTE STREAMS

The solid wastes produced in petroleum refineries fall into three general waste stream categories: process solids, waste treatment solids and miscellaneous nonprocess solids. The sources of major contaminants in and the existing refinery control technologies for these three categories of waste are listed in Table 4-10.

4.3.1 Stream No. 1, Process Solids

The process solid wastes originate from various refinery subunits/operations (e.g., crude oil storage, alkylation, hydrotreating, etc.). The chemical composition of the process sludges is a function of the source/operation and in some cases would vary among refineries depending on the type of crude oil processed (e.g., composition of sludges from crude oil storage). Some median values and ranges of concentration for selected constituents for three process wastes (spent catalyst, coker fines and crude oil storage bottom sediments) are presented in Table 4-11. As indicated in this table, these solid wastes contain heavy metals, phenols and oils (in the case of crude oil storage tank bottoms). In addition to the constituents shown in the table, both the spent catalyst and the coker fines are expected to contain a variety of organic constituents, including some highly hazardous substances (see Chapter 7.0).

The nature and quantities (production per unit of raw material handled) of process solids produced in a refinery would differ from those in a coal conversion plant primarily because of the differences in the nature of the raw materials used (oil vs. coal) and the greater diversity and complexity of the processing steps employed in the refinery. Because of the simpler nature of the operation, there would be fewer sources of process solid wastes in a coal conversion plant and these would include coal preparation wastes (refuse), coal/char fines and ashes produced in the gasification step and spent catalysts

TABLE 4-10. REFINERY SOLID WASTE STREAMS(16)

Stream No.	Process/Waste Stream	Major Sources	Major Constituents/ Contaminants	Existing Control Technology
1	Process solids	Crude oil, intermediate and product storage tank bottom sludges; spent catalysts from catalytic cracking and hydrotreating; fines from cokers, acid and alkali sludges from sweetening and processing (e.g., alkylation); miscellaneous process chemicals	Oils, trace elements (As, Cd, V, Pb, Se, etc.) phenols, acids, alkali, miscellaneous process chemicals; inerts (silt, clay, etc.), water	Landfilling and landspreading (primarily for oily wastes), on-site or off-site processing for material recovery (e.g., catalyst reclamation), storage in lagoons and evaporation ponds, energy recovery (e.g., incineration of oily wastes)
2	Waste treatment solids	API separator and flotation sludges; sludges from biological treatment; chemical sludges (lime, alum, etc.) from waste water treatment; cooling tower sludge; sludges from air pollution control processes (e.g., scrubbing for SO_2 control)	Oils, phenols, heavy metals, waste treatment chemicals, biomass (biological flow), inerts, water	Processing to reduce volume (e.g., filtration, thickening), landfilling and landspreading; incineration; storage in lagoons, evaporation ponds and drying beds
3	Miscellaneous non-process solids	Process and cooling water treatment sludges; maintenance wastes, general plant/ office refuse	Inerts (silts, sand, etc.) water treatment chemicals/precipitates (lime, calcium carbonate, etc.), oil, metals, papers, etc.	Storage in lagoons and evaporation ponds, landfilling, incineration (for refuse)

TABLE 4-11. PROCESS SOLIDS CHARACTERISTICS[18] [MEDIAN VALUE (RANGE)]

Constituents mg/kg (dry)	Spent Catalyst	Coker Fines	Crude Oil Storage Tank Sediment
Phenol	2.1 (0.3-72)	2.0 (0.4-2.7)	15.8 (6.1-21)
Cyanide	0.12 (0.01-1.44)	0.001 (0.00025-0.001)	0.0012 (.00025-0.8)
Se	0.01 (0.01-19.1)	0.01 (0.01-1.6)	0.03 (0.01-1)
As	1.0 (0.05-4.0)	2.0 (0.2-10.8)	21.1 (5.8-53)
Hg	0.0004 (0.0005-0.16)	0.04 (0.0004-0.2)	0.0026 (0.0013-0.25)
Be	0.5 (0.025-1.4)	0.005 (0.0025-0.5)	0.0026 (0.0013-0.25)
V	240 (74.4-1724)	455 (500-3500)	17.4 (5-62)
Cr	71 (12.3-190)	0.02 (0.02-7.5)	19.4 (1.9-75)
Co	6.6 (0.25-37)	4.0 (0.2-9.2)	14.8 (3.8-37)
Ni	241 (47.5-1000)	580 (350-2200)	16.2 (12.8-125)
Cu	17.5 (4.1-336)	4.0 (3.5-5.0)	65.4 (18.5-194)
Zn	39 (19-170)	14 (0.2-20)	145 (22.8-425)
Ag	1.8 (0.5-3.0)	0.01 (0.01-3.0)	0.19 (0.03-1.3)
Cd	0.003 (0.001-0.5)	1.0 (0.015-2.0)	0.31 (0.25-0.42)
Pb	50 (10-195)	13.0 (0.5-29)	18.9 (10.9-338)
Mo	6.3 (0.5-21.6)	0.1 (0.1-25)	6.3 (0.25-95)
Ammonium Sulfate (as NH_4^+)	0.1	0.7	2
Benzo-a-Pyrene	0.005 (0.0002-1.5)	0.002 (0.002-0.005)	0.11 (0.03-0.06)
Oil (wt %)	0.21 (0.01-0.81)	0.001 (0.001-1.34)	47.4 (21-83.6)
Water (wt %)	0	0	13.3 (1-20)

and sludges from gas purification and upgrading. Even though some of the process solids encountered in refineries would not have very close counterparts in coal conversion plants, the existing refinery control technologies (landfilling, incineration and material recovery) would be applicable to the management of certain solid waste streams in a coal conversion plant (see Section 6.3).

4.3.2 Stream No. 2, Waste Treatment Solids

As indicated in Table 4-12, major sources of waste treatment solids in a refinery are sludges from API separators, flotation units, biological wastewater treatment, water treatment and air pollution control. Table 4-12 presents some median values and ranges of composition of three types of waste treatment solids in a refinery (API separator, air flotation and waste biosludge). As indicated in the table, a range of values have been reported for the listed constituents, reflecting differences in the nature of wastewaters generated and the operating conditions in different refineries. For example, the reported oil and water contents of the API separator sludges vary from 3 to 60 wt % and from 7 to 98 wt %, respectively. The sludges from the API separator and flotation units are characteristically high in the content of oil, phenols and certain heavy metals (e.g., chromium which is used largely for corrosion control).

When biological processes are employed for the treatment of aqueous wastes, the degradation of organics and the physical entrapment and settling of suspended particles result in the production of the "biosludge." Sludges produced in the activated sludge and trickling filtration processes are settled in the "final" clarifiers which follow the aeration tank or the filter. In the activated sludge process a portion of the settled sludge is recycled to the aeration tank and the "excess" sludge is "wasted." Sludges removed from final clarifiers typically contain 2% to 5% solids with the solids generally containing 50% to 70% "volatile" matter. When lagoons and stabilization basins are used for biological treatment, the biological sludge produced and the settleable matter in the raw wastewater settle to the bottom; the degradable material in the settled sludge undergoes aerobic and/or anaerobic decomposition. Depending on the nature and quantity of the solids in the raw wastewater and the lagoon design, periodic cleaning of the lagoons to remove

TABLE 4-12. EFFLUENT TREATMENT SOLIDS CHARACTERIZATION(18)
[MEDIAN VALUE (RANGE)]

Constituents mg/kg (dry)	API Separator Sludge	Air Flotation Residue	Waste Biosludge
Phenol	13.6 (3.8-156.7)	6.5 (3.0-210)	4.5 (1.7-10.2)
Cyanide	0.001 (6×10^{-5}-51.4)	0.28 (0.01-1.1)	0.001 (0.0001-19.5)
Se	0.001 (0.0005-7.6)	2.0 (0.1-4.2)	0.01 (0.01-5.4)
As	6.2 (0.1-32)	2.0 (0.05-10.5)	3.8 (1.0-6.0)
Hg	0.4 (0.04-6.2)	0.27 (0.07-0.89)	0.18 (0.004-1.28)
Be	0.0025 (0.0012-0.24)	0.0025 (0.0012-0.25)	0.0013 (0.0013-0.002)
V	9,8 (1.0-48.5)	0.05 (0.05-0.15)	0.05 (0.012-5.0)
Cr	253 (0.1-6790)	140 (28-260)	300 (0.05-475)
Co	5.7 (0.1-26.2)	2.0 (0.13-67.5)	0.2 (0.05-1.4)
Ni	19.3 (0.25-150.4)	0.025 (0.025-15)	0.025 (0.013-11.3)
Cu	18.6 (2.5-550)	710 (0.05-21.3)	9.5 (1.5-11.5)
Zn	298 (25-6596)	85 (10-1825)	122 (3.3-225)
Ag	0.45 (0.05-3)	0.25 (0.0013-2.8)	0.3 (0.1-0.5)
Cd	0.42 (0.024-3)	0.005 (0.0025-0.5)	0.3 (0.15-0.54)
Pb	26 (0.29-1290)	7.5 (2.3-1250)	5.0 (1.2-17)
Mo	5 (0.25-30)	0.05 (0.025-2.5)	2.5 (0.25-2.5)
Ammunium Sulfate (as NH_4^+)	6.5 (0.05-30)	9 (8.5-210)	21 (6.5-30)
Benzo-a-Pyrene	0.004 (0.0025-4.5)	0.002 (0.004-1.75)	0.003 (0.002-0.005)
Oil (wt %)	22.6 (3.3-59.8)	12.5 (2.5-16.9)	0.28 (0.01-0.53)
Water (wt %)	53 (7-98)	82 (30-99)	87 (56-95)

the settled sludge may be necessary. Certain elements (e.g., heavy metals) and refractory organics which may be present in the raw wastewater at relatively low concentration levels tend to concentrate in the biosludges. High concentrations of such substances in the sludge may eliminate certain options for sludge disposal (e.g., use as fertilizer on agricultural soils). Biosludges from refineries have been reported to contain Cr and Zn values of 540 and 200 mg/kg of dry sludge, respectively(18). Heavy metal concentration is especially pronounced when anaerobic digestion is used for the stabilization and thickening of "primary" and "secondary" sludges.

The characteristics of the biosludges from coal conversion facilities are expected to be generally similar to those of petroleum refinery biosludges. However, coal conversion biosludges may contain refractory organics which are chemically different from petroleum biosludges. The inorganic component of coal conversion biosludges (e.g., trace elements) may also differ. Despite differences in the composition of refinery and coal conversion waste treatment solids, the existing refinery control technologies (sludge concentration followed by landfilling, landspreading or incineration) would be applicable to the management of waste treatment solids in coal conversion plants. (See Section 6.3.)

4.3.3 Miscellaneous Nonprocess Solids

Table 4-13 presents waste characterization data for four types of miscellaneous nonprocess solid wastes in a refinery (lime sludge from boiler water treatment, maintenance waste, cooling tower sludge and sediments from settling of surface runoff from the plant areas). Except for some contamination with certain substances associated with the refining operations (e.g., oils, phenols and heavy metals), the characteristics of these waste streams and the technology for their controls would be similar to their counterparts in other industries (including coal conversion). Those technologies which are also applicable to the management of process and waste treatment solids (storage in lagoons, landfilling, etc.) are reviewed in Section 6.3.

TABLE 4-13. GENERAL WASTES CHARACTERISTICS(18)
[MEDIAN VALUE (RANGE)]

Constituent mg/kg	Spent Lime from Boiler Feed Water Treatment	Maintenance Waste	Silt from Storm Water Runoff	Cooling Tower Sludge
Phenol	2.1 (0.05-3.6)	13.3 (8-18.5)	7.5 (6.3-8.6)	3.5 (0.6-7.0)
Cyanide	0.001 (2×10^{-5}-1.28)	1.7 (0.0004-3.3)	1.72 (0.34-3.1)	0.1 (0.0005-17.2)
Se	0.01 (0.01-12.2)	27.2 (2.4-52)	1.7 (1.1-2.2)	0.15 (0.01-2.5)
As	0.1 (0.05-2.6)	10.6 (10.2-11)	5.5 (1.0-10.0)	8.2 (0.7-21)
Hg	0.04 (0.004-2.73)	1.9 (0.13-3.6)	0.30 (0.23-0.36	0.09 (0.004-3.35)
Be	0.0012 (0.001-0.002)	0.20 (0.05-0.34)	0.0019 (0.0012-0.0025)	0.0013 (0.001-0.2)
V	0.05 (0.007-31.6)	25 (0.7-50)	69 (25-112)	7.8 (0.12-35)
Cr	2.2 (0.025-27.9)	311 (310-311)	354 (32.5-675)	554 (181-1750)
Co	0.005 (0.002-1.3)	1.6 (0.2-3.0)	11.2 (11.0-11.3)	1.3 (0.38-7)
Ni	2.5 (0.13-22.5)	116 (61-170)	85 (30-140	6.8 (0.25-50)
Cu	3.8 (0.22-63.2)	71 (67-75)	28.3 (14.8-41.8)	50 (13-363)
Zn	15.0 (2.0-121)	194 (91-297)	230 (60-1000)	675 (118-1100)
Ag	0.05 (0.05-0.7)	0.005 (0.0007-0.01)	0.5 (0.5-0.5)	0.28 (0.01-1.6)
Cd	0.003 (0.0012-0.3)	1.3 (1.0-1.5)	0.22 (0.01-0.42)	0.3 (0.06-0.6)
Pb	3.8 (0.01-7.3)	78 (0.5-155)	53.3 (20.5-86)	38 (1.2-89)
Mo	0.025 (0.0025-0.05)	6.5 (1-12)	6.9 (6.3-7.5)	1.1 (0.25-2.5)
Ammonium Salts (as NH_4^+)	0.015 (0.005-5.0)	8 (5-11)	1.0	6.3 (0.07-14)
Benzo-a-Pyrene	0.002 (0.002-0.002)	2.2 (0.7-3.6)	1.27 (0.03-2.5)	0.004 (0.003-0.8)
Oil (wt %)	0.32 (0.04-0.49)	10.7 (8.3-13)	3.9 (2.2-5.5)	0.44 (0.07-4.0)
Water (wt %)	59 (5-91.8)	53 (42-64)	25 (20-29.7)	75.4 (50-883)

5.0 CHARACTERISTICS OF COAL CONVERSION WASTE STREAMS

The characterization of coal conversion waste streams was undertaken to identify those streams which have counterparts in petroleum refining, and/or can be processed by the refining control technologies.

5.1 COAL CONVERSION PROCESSES

Of a significantly large number of processes which have been suggested for the production of low/medium Btu gas, high Btu gas and liquid fuel from coal, only a few have attained or are approaching commercial status. Many of the processes, especially those which are still in early developmental stages, have not been operated on a meaningfully large scale or for a sufficient length of time to allow detailed and meaningful characterization of waste streams associated with any commercial scale process application.

To establish the processes of interest to the program, nine low/medium Btu gasification, eight high Btu gasification and three liquefaction processes were reviewed (see Table 5-1). Based on the considerations of (a) availability of data on waste stream characteristics, (b) attainment of, or nearness to commercial status, (c) representation of integrated operations producing upgraded or refined fuels and (d) avoidance of duplication with other EPA projects, three processes were selected for detailed review of the available data on waste stream characteristics. These processes are Koppers-Totzek (low/medium Btu gasification), dry ash Lurgi (high Btu gasification) and COED (liquefaction). It is recognized that because of the differences among the individual processes in the three technology categories, there would be significant differences in the types and characteristics of the waste streams from the processes in each category and that no single process can represent the category. For example, in the case of liquefaction, the waste streams from hydrogenation processes, such as the H-Coal process, could drastically differ from those from pyrolysis processes such as COED. The selection of COED as an example of liquefaction processes is for analysis purposes only and does not imply that the COED wastes necessarily typify liquefaction wastes.

TABLE 5-1. COAL CONVERSION PROCESSES REVIEWED

Low/Medium Btu Gasification	High Btu Gasification	Liquefaction
Chapman (Wilputte)	Bigas	COED
Coalex	CO_2-Acceptor	SRC
Foster Wheeler/Stoic	Cogas	H-Coal
Koppers-Totzek	Hydrane	
Reiley Morgan	Hygas	
Texaco	Lurgi (dry ash)	
Wellman-Galusha	Lurgi (slagging)	
Winkler	Self-agglomerating ash	

The Koppers-Totzek (K-T) process is considered to be one of the most likely low-medium Btu gasification processes to be used in commercial applications in the U.S. for synthesis gas production. Commercial installations using the K-T process have been in operation in other countries for a number of years and some process/waste stream composition data are available for this process.

The dry ash Lurgi is considered a commercial process and, compared to any of the other processes, considerably more operating experience is available on this process. Essentially all proposed designs for commercial SNG facilities in the U.S. are based on the Lurgi technology.

COED was selected as the example for the liquefaction technology since not only are considerable data available for the process but the proposed designs also feature several processes (e.g., product separation and hydrotreating) which would be used in connection with a number of other liquefaction schemes. The COED process, moreover, produces liquid fuel(s) which can be processed to produce petroleum fuel substitutes. The Solvent Refined Coal (SRC) process was not selected to represent the liquefaction technology because most of the available pilot plant data for the process are for the "SCR-I" which produces a solid fuel and is considered essentially a coal deashing/

desulfurization operation; also it is being treated in-depth by related EPA studies. The "SCR-II" process, which is designed to produce liquid fuel as the primary product, is in the very early developmental stage and few data are currently available on this version of the SRC process.

Figure 5-1 presents a generalized flow diagram for coal conversion systems with the major waste streams identified (numbered 1 through 18). A brief review of the characteristics of the identified streams and comparison of their characteristics with their refinery counterparts follow.

5.2 GASEOUS WASTE STREAMS

Table 5-2 lists the gaseous streams identified in Figure 5-1 along with their source(s) and major contaminants. Stream No. 1 (Raw Product Gas) is not a waste stream; it has, however, been included here because in some respects it is similar to the refinery process sour gases (see Section 4.2.1). The coal conversion gaseous streams which have been found to have possible counterparts in refineries are: raw product gas, acid gases, raw fuel gas, fugitive emissions, flue gas and cooling tower gas. Streams 8 and 9 have no refinery counterparts.

5.2.1 Stream No. 1, Raw Product Gas

Before the quenched raw product gas is further processed or consumed directly, it is usually necessary to remove the sulfur compounds in the product gas. Table 5-3 presents the characteristics of raw product gases (after quenching and dust removal) from the Lurgi and K-T gasifiers. For comparison purposes, the composition data for process sour gases from petroleum refineries are also given.

As can be seen from the data in Table 5-3, despite certain general similarities (e.g., presence of H_2S and CO_2) there are significant differences in the characteristics of the quenched product gas and refinery process sour gases. In general, the quenched product gas:

- Contains higher levels of H_2, CO, and CO_2
- Has much lower levels of H_2S
- Is at a much higher temperature and (in the case of Lurgi) at higher pressure

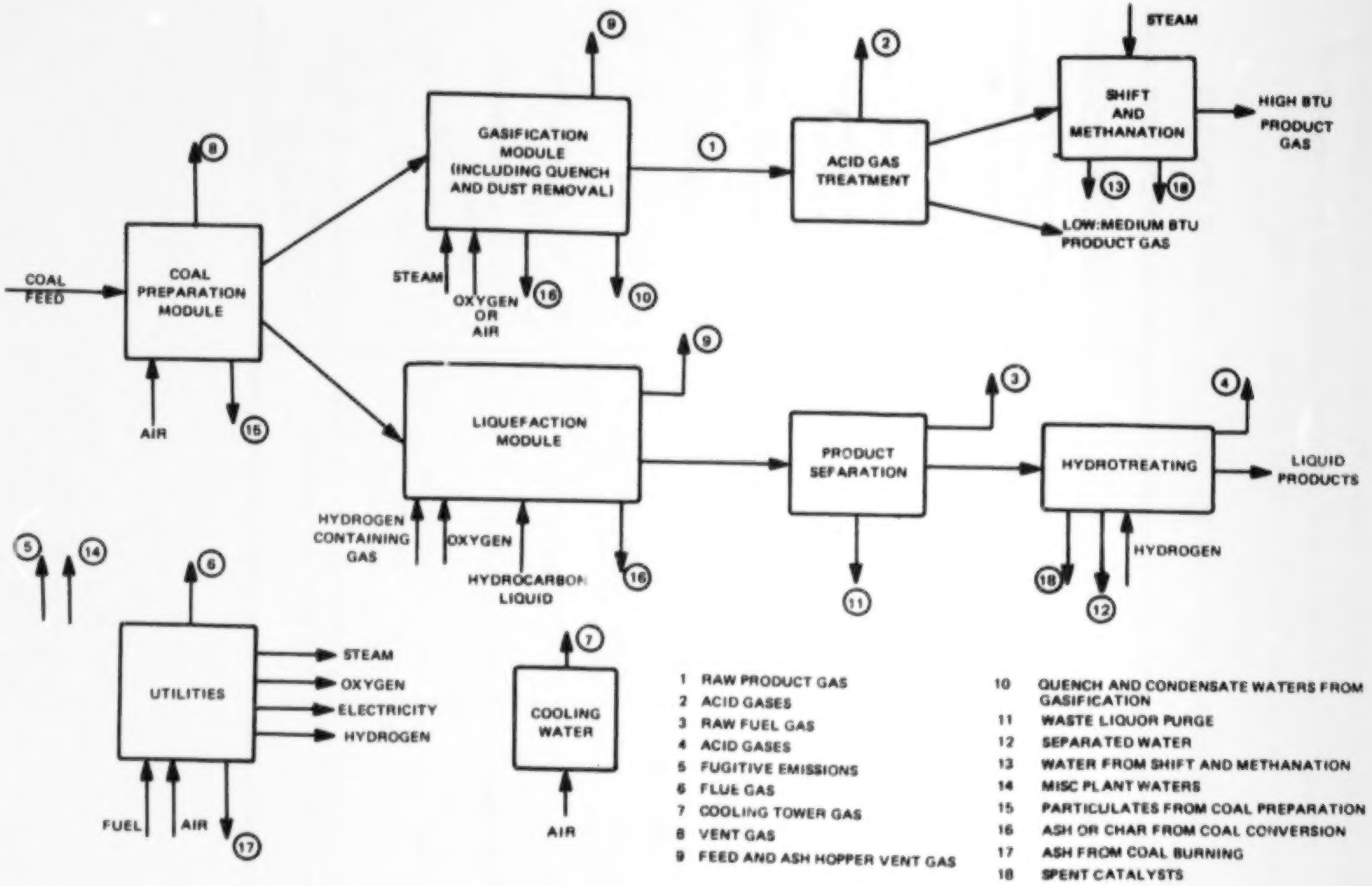
COAL FEED
COAL PREPARATION MODULE
AIR
⑧
⑮
GASIFICATION MODULE (INCLUDING QUENCH AND DUST REMOVAL)
STEAM
OXYGEN OR AIR
⑨
⑯
⑩
①
ACID GAS TREATMENT
②
STEAM
SHIFT AND METHANATION
HIGH BTU PRODUCT GAS
⑬
⑱
LOW:MEDIUM BTU PRODUCT GAS
LIQUEFACTION MODULE
HYDROGEN CONTAINING GAS
OXYGEN
HYDROCARBON LIQUID
⑨
⑯
PRODUCT SEPARATION
③
⑪
HYDROTREATING
④
LIQUID PRODUCTS
HYDROGEN
⑱
⑫
⑤
⑭
UTILITIES
⑥
FUEL
AIR
⑰
STEAM
OXYGEN
ELECTRICITY
HYDROGEN
COOLING WATER
⑦
AIR
1 RAW PRODUCT GAS
2 ACID GASES
3 RAW FUEL GAS
4 ACID GASES
5 FUGITIVE EMISSIONS
6 FLUE GAS
7 COOLING TOWER GAS
8 VENT GAS
9 FEED AND ASH HOPPER VENT GAS
10 QUENCH AND CONDENSATE WATERS FROM GASIFICATION
11 WASTE LIQUOR PURGE
12 SEPARATED WATER
13 WATER FROM SHIFT AND METHANATION
14 MISC PLANT WATERS
15 PARTICULATES FROM COAL PREPARATION
16 ASH OR CHAR FROM COAL CONVERSION
17 ASH FROM COAL BURNING
18 SPENT CATALYSTS

Figure 5-1. Generalized Flow Plan for Coal Conversion Process (not all input or discharge lines are applicable to all processes)

As will be discussed in Section 6.1, these differences in gas characteristics would require the use of different gas processing methods for the removal of sulfur components from the raw and by-product acid gas streams.

TABLE 5-2. MAJOR GASEOUS WASTE STREAMS FROM COAL CONVERSION PROCESSES

Stream No.	Stream	Source(s)	Major Contaminants
1	Raw Product Gas	Product of gasification of coal after quench and dust removal	Primarily sulfur compounds, HCN and naphthalene (in high Btu gasification CO_2 is considered a contaminant and is removed in the acid gas treatment section)
2	Acid Gases (gasification)	Acid gas removal module	Sulfur compounds, CO, hydrocarbons and solvents
3	Raw Fuel Gas (liquefaction)	Product separation	Sulfur compounds and HCN
4	Acid Gases (liquefaction)	Hydrotreating	Sulfur compounds
5	Fugitive Emissions	Compressors, drains, storage tanks, etc.	Hydrocarbons
6	Flue Gas	Utility boilers	SO_2, CO, HC, NO_x and particulates
7	Cooling Tower Gas	Cooling towers	Volatile hydrocarbons, H_2S and NH_3
8	Vent Gas	Coal preparation (including crushing, drying and storage)	Particulates, flue gas constituents
9	Feed and Ash Hopper Vent Gas	Pressurization of feed and ash lockhoppers	Particulates, volatile hydrocarbons, CO and sulfur compounds

TABLE 5-3. COMPARISON OF THE COMPOSITIONS OF COAL GASIFICATION QUENCHED RAW PRODUCT GAS AND REFINERY SOUR GAS*

Gas Stream Components/Parameters	Lurgi	K-T	Refinery Process Sour Gases†
H_2	39.1	32.74	-
O_2	0.6	-	-
CO	17.3	57.35	-
CH_4	9.4	-	8.4
CO_2	31.2	7.05	1.9 - 4.9
C_2H_6	0.7	-	4.36 - 5.2
H_2S	1.1	1.59	16.4 - 62.5
CH_3SH	-	-	-
COS	-	0.114	-
N_2 + Ar	0.6	1.16	-
NH_3	0.18	-	-
HCN	2.8	-	-
Naphthalene	0.68	-	-
Temperature, °K (°F)	727 (850)	1750 (2700)	320 (122)
Pressure, MPa (psia)	2.1 (300)	0.1 (15)	0.15 (22)

*Except as noted, all values in mole %.

†From Table 4-2.

5.2.2 Stream No. 2, Acid Gases

The processes presently in use to remove acid gases from coal gasification plant raw product gases generally involve the chemical or physical absorption of the acidic components in a suitable liquid with subsequent desorption at a lower pressure (and in some instances at a higher temperature).

Two of the acid gas treatment processes which have been used in connection with gasification processes and for which some operating data are available are the Rectisol and Benfield processes. The characteristics of the recovered gas streams from these processes are presented in Table 5-4 and compared with their refinery counterpart. As can be seen, large differences exist in the concentrations of CO_2 and H_2S in the acid gases from coal gasification and refineries. These differences in composition will require different processes or different operations for both sulfur recovery and tail gas cleanup than those in use at refineries (see Section 6.1).

TABLE 5-4. COMPARISON OF THE RECOVERED ACID GAS FROM RECTISOL AND BENFIELD WITH THOSE IN REFINERIES

Characteristics	Rectisol (Operating on K-T Gas)	Benfield (Operating on Lurgi Gas)	Refinery* (Range for Different Processes)
CO_2, mole %	75	98	4.6 - 46.1
H_2S, mole %	22	2	50.3 - 91.4
COS, mole %	3	-[†]	-
Temp., °K (°F)	313 (105)	383 (230)	313 (105)
Press., MPa (psia)	0.1 (15)	2.1 - 7.6 (300 - 1100)	0.15 (22)

*From Table 4-2

[†] Dash indicates no data on this compound has been reported.

5.2.3 Stream No. 3, Raw Fuel Gas from Liquefaction

In the liquefaction of coal, raw fuel gases (i.e., gases which are usually used either to fire process and utility units or are sold) are separated from the liquid product, and solid wastes, in the "product separation module." The amount of gas present varies with the specific liquefaction process (values of 54, 52 and 12 wt. %, based on input to the product separation module, have been reported for COED, SRC and H-Coal processes, respectively). The raw fuel gas will have to be treated for removal of sulfur compounds prior to use. In terms of its major constituents, the liquefaction raw fuel gas is expected to be similar to Stream No. 1, raw product gas.

5.2.4 Stream No. 4, Acid Gases from Hydrotreating

In the COED liquefaction process acid gases are generated as a result of hydrotreating of the liquid product. (The H-Coal and SRC processes do not incorporate hydrotreating.) The objective of hydrotreating is to reduce sulfur, oxygen and nitrogen compounds and to hydrogenate unsaturated hydrocarbons and aromatics. Sour gas is produced which should be similar to that from refinery hydrotreating operations.

Table 5-5 presents the composition of gases produced by hydrotreating COED product oil. This stream is very small (less than 2.7 Nm^3/min for a 22,000 tonne/day plant or 100 scfm for a 24,000 ton/day plant) and in a commercial facility would probably be combined with other gas streams for treatment.

TABLE 5-5. CHARACTERISTICS OF HYDROTREATING ACID GASES FOR THE COED PROCESS*

Component	wt %†
N_2	0.82
H_2	2.15
CO_2	8.82
CO	74.69
H_2	4.77
CH_4	5.95
H_2S	0.69
NH_3	2.10
Temp., °K (°F)	315 (100)
Press., MPa (psia)	0.1 (16)

*Actual comparative data not available for the hydrotreating acid gases produced in refineries.

†Except for temperature and pressure.

5.2.5 Stream No. 5, Fugitive Air Emissions

A variety of sources may account for fugitive emissions in coal conversion plants. Among these are: compressors, valves, flanges, wastewater and solids handling units, etc. The major pollutants present in these emissions consist of the materials handled (primarily hydrocarbons, sulfur compounds, CO, etc.). Similar sources of emissions are present in refineries. The actual compositions of the fugitive emissions vary widely, depending primarily on the emission source and the nature of product handled.

Control technologies to reduce fugitive emissions will depend on the source. Certain sources, such as vents and storage tanks, may be controlled by the use of vapor collection and recovery techniques which are currently employed in some refineries and other industrial facilities.

5.2.6 Stream No. 6, Flue Gas

Flue gases in coal conversion plants would originate primarily from the central steam plant. Some process sections (e.g., hydrotreating in the COED liquefaction scheme) contain small heaters or boilers which would also generate flue gas emissions. The composition of the flue gas would depend primarily on the type of fuel used. Process developers may choose to use some of the "clean" coal conversion products as the fuel or burn coal or char directly. The flue gas emission controls required in a coal conversion plant would be dependent on the type of fuel used.

The utility boiler and process furnaces in a refinery are generally oil or fuel gas fired; characteristics of the flue gas emissions from these units would be different from those encountered in coal conversion plants. Accordingly, the flue gas control technology used in refineries would not be directly applicable to the management of flue gas emissions in coal conversion plants. The required technologies for the control of flue gas emissions from the combustion of coal and char in coal conversion plants would be those which have been developed in other industries, primarily the utility industry. Because of the inapplicability of the refinery control technology, Stream No. 6 has been omitted from further consideration in this report.

5.2.7 Stream No. 7, Cooling Tower Gas

Emissions from cooling towers primarily contain water vapors and mists. Depending on the source of the makeup water used, the emissions may also contain volatile organics, H_2S and NH_3. (In some refineries, treated process wastewaters, such as stripped sour waters or effluent from biological treatment, are used as the cooling water makeup.) The water vapors and mists emitted in the drift can contain salts and organics. In refineries, the emissions from cooling towers are controlled through proper cooling tower design and control of the quality of the water used as makeup. In coal conversion plants, treated process wastewaters would also likely be used as cooling water makeup, and the cooling tower emissions can be controlled in a similar manner.

5.2.8 Stream No. 8, Coal Preparation Vent Gases

For the Lurgi, Koppers-Totzek and COED processes, the coal preparation operations include crushing, drying and storage. The coal preparation requirements generally vary with the specific coal conversion process. For instance, Lurgi requires no coal drying while, depending on the coal used, both K-T and COED may require coal drying. The composition of vent gases from coal preparation would also vary depending on the characteristics of the feed coal and the degree of crushing and drying reuqired. (The coal sizes for K-T and COED processes vary from less than 0.07 mm to 45 mm.)

Although no actual data have been reported on the composition of the vent gases for pretreatment operations, these gases are expected to contain such classes of contaminants as: particulates, volatile hydrocarbons, SO_2, CO and NO_x. Gases from crushing and storage will primarily contain particulates, while those from drying would also contain combustion products. The quantities would depend upon the fuel used and the operating conditions of the heater.

No counterpart to coal preparation vent gases has been identified in refining operations. The control technologies which would be used for the vent gases would most likely be those commonly employed in the mining and utility industries. Examples of such technologies include use of filter bags for particulate control, incineration for the destruction of organics and combustion modification for the control of NO_x emissions.

5.2.9 Stream No. 9, Feed and Ash Hopper Vent Gas

Gases used to pressurize feed and ash lockhoppers may contain particulates, volatile hydrocarbons and components present in the gasifier gas. A feed lockhopper is not used in processes which employ pneumatic feeding (e.g., COED) or operate at atmospheric pressure (e.g., Koppers-Totzek).

No counterparts to lockhopper vent gases appear in refineries (or in other industries). Control of emissions from this source would, by necessity, be of unique design incorporating return of the gases to the main gas stream as well as the use of inert gases (e.g., carbon dioxide) for pressurization.

5.3 LIQUID WASTE STREAMS

Table 5-6 lists the major liquid waste streams associated with coal conversion systems (the stream numbers correspond to those in Figure 5-1). Only the first stream listed in the table (Stream No. 10, quench and condensate waters from gasification) would have a counterpart in petroleum refining. Stream Nos. 11 and 12 have similar composition to refinery wastewaters; however, the technologies proposed for use in the coal liquefaction system (i.e., injection of these waters into the pyrolyzer) is very unique and different from the refinery control technologies. Stream No. 13 has no counterpart in refineries (see Section 5.3.4). Stream No. 14 has counterparts in refineries and in many other chemical process industries, and their control is not unique to coal conversion plants or refineries.

Discussions of each of the streams listed in Table 5-6 follows.

5.3.1 Stream No. 10, Quench and Condensate Waters from Gasification

The condensate stream from coal gasification processes includes quench waters as well as condensates removed in gas cooling. The composition of condensate waters from coal gasification is dependent upon the conditions within the gasifier. In general, gasifiers (e.g., K-T) which operate at higher temperatures produce less tars and oils than lower temperature gasifiers. Table 5-7 presents the compositions of condensate waters from the Lurgi and K-T processes. The table also contains the characteristics of

TABLE 5-6. MAJOR LIQUID WASTE STREAMS FROM COAL CONVERSION PROCESSES

Stream No.	Stream	Source(s)	Major Contaminants
10	Quench and condensate waters from gasification	Quenching and gas cooling	Phenols, ammonia, sulfur compounds and heavy metals
11	Waste liquor purge from product separation (liquefaction)	Product separation and recovery	Phenols, oils, ammonia, sulfates, and heavy metals
12	Separated water from hydrotreating (liquefaction)	Hydrotreating	Ammonia, sulfates, and heavy metals
13	Water from shift and methanation	Shift and methanation	Dissolved gases, traces of sulfur, nitrogen, hydrocarbons and heavy metals
14	Miscellaneous plant waters	Storm water run-off, boiler blow-down, etc.	Small amounts of solids, phosphates, sulfates and heavy metals

TABLE 5-7. COMPARISON OF THE CONDENSATES FROM GASIFICATION AND REFINERIES

	Lurgi		K-T	Refinery*	
Characteristic	Inlet to Tar Separator	Inlet to Oil Separator	Combined Stream	Sour Water	Oily Water
pH	9.8	8.5	8.9	8.6	8.2
TDS, mg/l	2770	1570	2769	1310	--
Sulfide, mg/l	47	831	--	2172	3550
Ammonia, mg/l	1700	17650	15	390	1930
Carbonate, mg/l	5644	29110	681	5244	320
Cyanide, mg/l	4	16	0.01	--	--
Chloride, mg/l	128	71	284	--	82
Phenols, mg/l	2200	1900	--	365	200

*From Tables 4-8 and 4-9.

refinery wastewaters for comparison. The major differences between coal gasification condensate and refinery wastewaters are in the amounts of phenols, ammonia and sulfides present. Generally, low to medium temperature gasification and liquefaction processes (e.g., Lurgi and COED) generate condensates with higher levels of ammonia and phenols and lower levels of sulfide than found in refinery sour waters. For high temperature gasification processes (e.g., K-T), low levels of ammonia are usually found in condensates (presumably coal nitrogen is oxidized in the gasifier).

5.3.2 Stream 11, Waste Liquor Purge from Product Separation

In the COED process the waste liquor purge from product separation contains waters generated in the pyrolysis stages. Estimates of the composition of these waters are presented in Table 5-8. Major contaminants in these waters are phenols, oils and heavy metals, nitrogen and sulfur compounds. In refineries a close counterpart of this stream does not exist due to the high levels of certain contaminants present in the purge stream which are unique to coal (e.g., heavy metals).

TABLE 5-8. COED WASTE LIQUOR PURGE STREAM COMPOSITION

Constituent	1st Stage Pyrolysis	2nd Stage Pyrolysis
Nitrogen (wt. % N)	0.05	0.93
Sulfur (wt. % S)	0.07	0.18
Phenol (wt. %)	0.00	0.38
Entrained Oil (wt. %)	--	0.00 - 0.5
Suspended Solids (wt. %)	0.49	1.09
pH	3.6	9.3

The purge gas pollution control technologies expected to be incorporated in the design of coal conversion plants would also be different than any technology used in the refining industry. For example, the COED process developer (the FMC Corporation) expects to recycle these waters to one of the pyrolysis stages.

Based on the consideration of the waste characteristics and the uniqueness of the control technology suggested for use in conjunction with the COED process, Stream No. 11 has been eliminated from further consideration.

5.3.3 Stream No. 12, Separated Water from Hydrotreating

Hydrotreating is used to remove sulfur and nitrogen from the product oil and to hydrogenate unsaturated compounds. Water separated from this process generally contains considerable quantities of sulfur and nitrogen compounds (see Table 5-9). This stream, like Stream No. 11, waste liquor purge, is expected to be recycled to the pyrolyzers and its sulfur and nitrogen components would eventually appear in waste liquor from product separation.

TABLE 5-9. HYDROTREATING SEPARATED WATER COMPOSITION

Constituent	Value
Carbon, wt %	0.8
Nitrogen, wt %	5.0
Sulfur, wt %	8.7
pH	9.3

5.3.4 Stream No. 13, Waters from Shift and Methanation

Essentially no characterization data have been reported for raw wastewaters produced as a result of shift conversion and methanation of the product gas from coal gasification. Shift conversion and methanation waters are expected to be relatively "clean" because of the nature of the operation and the gas handled. Most major pollutants in the product gas (e.g., ammonia, tars, oil, etc.) have been removed prior to shift conversion and methanation. Small amounts of dissolved gases with traces of sulfur, nitrogen and hydrocarbon (other than methane) compounds may be present. The counterpart of Stream No. 13 in refineries would be the refinery "clean" waters.* Because of the "clean" nature of Stream No. 13, the control technology for the stream in a coal conversion plant will be minimal. The stream will probably be added to the wastewaters after oil-water separation and treated jointly in the biological treatment plant, or treated for use as boiler or cooling tower makeup.

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*When on-site hydrogen production is employed in refineries (for hydrotreating), shift and methanation would be used in the hydrogen plant. The condensate from such shift and methanation, however, is a very "clean" stream since protection of the catalyst requires that nearly all sulfur and nitrogen compounds be removed from the feed gas by prior treatment.

5.3.5 Stream No. 14, Miscellaneous Plant Wastewaters

Miscellaneous sources of wastewater in coal conversion plants include: boiler blowdown, cooling tower blowdown, storm water runoff, and sanitary sewage. Similar streams exist in refineries and the methods of handling and controlling these wastewaters (e.g., settling in retention ponds, use as process water, biological treatment, etc.) would not be unique to coal conversion plants or to refineries but are used in a variety of industrial production facilities.

5.4 SOLID WASTE STREAMS

Solid waste streams identified in Figure 5-1 are listed in Table 5-10. The source(s) and major constituents of these streams are also presented. Streams No. 15 and 16 (spent catalyst and sludges, respectively) are the only streams with refinery counterparts. Each of the coal conversion solid waste streams listed in Table 5-10 is discussed in the following subsections.

TABLE 5-10. SOLID WASTE STREAMS FROM COAL CONVERSION PLANTS

Stream No.	Stream	Source(s)	Major Contaminants
15	Spent Catalyst	Shift, methanation hydrotreating	Base metals, hydrocarbons, miscellaneous accumulated contaminants (such as sulfuric and organic nitrogen compounds
16	Sludges	Wastewater treatment	Tars/oils, biosludge
17	Particulates from coal preparation	Coal preparation	Coal fines, inerts
18	Ash or char from coal conversion	Gasification or liquefaction	Ash and heavy metals
19	Ash from coal burning	Boilers	Ash

5.4.1 Stream No. 15, Spent Catalysts

Some of the catalysts used in coal conversion are the same as those used in refining operations. For example, cobalt-molybdate catalysts are used in the hydrotreating of product oil in the COED process and in refinery hydrotreating. The contaminants, which will be present on the spent hydrotreating catalysts, would differ considerably between coal conversion systems and refineries due to feedstream differences (coal-derived products vs. products derived from crude oil). The technologies presently employed by refiners (resource recovery, landfilling, landspreading) will most likely find application in coal conversion plants.

5.4.2 Stream No. 16, Sludges

Tar and oily sludges are produced in the treatment of oily wastewaters by gravity separation and/or flotation and in emulsion breaking. Depending on the system design and the nature of the raw wastewater and emulsions, these sludges can contain a substantial amount of water. Sludges from the API separators in petroleum refineries have been reported to contain from 7% to as much as 98% oil(18). The characteristics of the organic fraction of the sludge would be similar to the bulk tars and oils produced in coal conversion processes. Because tars and oils are removed from the raw gas in a quenching operation, tar and oily sludge would contain high levels of coal-derived organic and inorganic particulate matter.

5.4.3 Stream No. 17, Particulates from Coal Preparation

The source of particulates from coal preparation will be the particulates removed by equipment used to control emissions from crushing, handling and storage operations. The composition of this stream will be somewhat similar to the feed coal composition. Some coal conversion processes can take these particulates (mostly coal fines) as feed; in other processes, the coal fines are rejected as waste or incinerated for heat recovery.

There is no refinery counterpart to coal preparation particulates. Controls to be used in coal conversion plants may include: briquetting and using as feed to the coal conversion processes, burning in a pulverized coal boiler or disposing with the ash or char from the conversion process.

5.4.4 Stream No. 18, Ash or Char from Coal Conversion

The ash or char remaining after coal conversion will comprise the major solid waste from coal conversion plants. The volume involved will be very large (dependent upon the ash content of the feed coal and the carbon conversion efficiency of the process). Data on the composition of the ash from the Lurgi process and the elemental analysis of char from the COED process are presented in Table 5-11. Due to differences in feedstocks (coal vs. oil) and operations, no counterpart to the ash or char stream exists in refineries. However, the solid waste management technologies employed in refineries and other industries (e.g., landfilling and landspreading) would be applicable to the control of the waste stream in coal conversion plants. Char generated in coal conversion plants may be used as a fuel for steam, for electricity generation, or further gasified (as in the Cogas process).

TABLE 5-11. ASH AND CHAR CHARACTERISTICS*

Constituent (wt. %)	Lurgi (ash)	COED (char)
Carbon	3.2	80.9
SiO_2	49.6	--
Al_2O_3	20.5	--
Fe_2O_3	17.2	--
CaO	2.1	--
MgO	1.0	--
S	1.3 (as SO_3)	0.5 (as S)
Cl	0.01	--
H	--	1.3
O	--	0.4
P	--	1.4

*No data available on the composition of the slag slurry for the K-T process; the composition of the slag, however, is expected to be similar to that of coal ash.

5.4.5 Stream No. 19, Ash from Coal Burning

Where coal is used as the boiler feed for steam and/or electricity generation, ash is the solid waste stream. The characteristics of this stream are dependent upon the type and composition of the coal employed and the boiler type used. Since refineries do not use coal for steam/electricity generation, Stream No. 18 has no counterpart in refineries. In coal conversion plants, the ash from coal burning can be disposed of (along with the ash from coal conversion) using such methods as landfilling.

6.0 REFINERY CONTROL TECHNOLOGIES AND THEIR APPLICABILITY TO COAL CONVERSION SYSTEMS

In this chapter the processes used by petroleum refineries for the control of gaseous, liquid and solid wastes are discussed and their applicabilities to coal conversion waste streams are evaluated.

6.1 GAS PROCESSING AND CONTROL OF GASEOUS EMISSIONS

Refinery gas processing and emission control technologies which may find applications in coal conversion plants include: acid gas treatment, sulfur recovery and tail-gas treating processes; incineration (flaring); and control devices for fugitive emissions.

6.1.1 Acid Gas Treatment Processes

In petroleum refineries, acid gas treatment consists of removal of H_2S and other sulfur compounds from (a) sour gases to produce clean-burning fuel, and (b) from feed gases to protect downstream unit operations. The removal of acid gases from the raw product gas in coal gasification and from raw fuel gas in coal liquefaction are carried out primarily to achieve the following:

- Removal of H_2S and other sulfur compounds to produce "clean fuels" and to protect downstream gas processing catalysts (e.g., methanation catalyst in high Btu gas production)
- Removal of CO_2 to produce high Btu gas suitable for long distance pipeline transportation.

H_2S and CO_2 may be removed either simultaneously ("nonselective") or separately ("selective"), depending on the specific acid gas removal process chosen and its design.

Selective processes produce a concentrated H_2S stream which can be treated in a Claus plant for sulfur recovery. In coal gasification applications where the feed gas has a high CO_2/H_2S ratio, nonselective processes would generate a stream containing nearly the same CO_2/H_2S ratio as the feed gas and hence require treatment by processes other than Claus (e.g., Stretford, which can handle dilute H_2S levels). In general, sulfur recovery from concentrated streams offers considerable economic advantage. The CO_2 stream generated in the selective processes may contain too high a level of residual H_2S for atmospheric discharge and hence may require additional treatment. The specific acid gas treatment process (selective or nonselective) to be used in a coal conversion plant should be selected with due consideration to the integration of the process with sulfur recovery and/or tail gas treatment and the overall economics of the sulfur management scheme.

Processes which are used in refineries for bulk acid gas removal from sour gases generally use solvents or solutions for the removal of acid gases. Depending on the process, the spent solution is regenerated by heating, depressurization or oxidation. The regeneration results in the production of a concentrated by-product gas stream which can be processed for sulfur removal and/or recovery. Solvent processes may be broadly classified as physical solvent processes, chemical solvent processes (amine based and carbonate based) and mixed solvent processes. The processes used in refineries and conversion facilities in each category and their key features are presented in Table 6-1. Redox systems such as Giammarco-Vetrocoke process, which are suitable for bulk acid gas removal and have been used for this purpose in the natural gas industry, are not considered here as no such applications have been reported in refineries. Redox systems, however, are used in refineries for tail gas treatment (see Section 6.1.3). As shown in Table 6-1, physical solvents offer good selectivity for removal of H_2S over CO_2 and can remove other sulfur and nitrogen compounds, water vapor, and some organics. Physical solvents are more effective and economical when high partial pressures of acid gases are encountered. Amine solvents are generally less selective than physical solvents and have higher energy requirements for regeneration. As the partial pressure of acid gas in the gas stream increases, the economy of amine systems declines. Mixed solvents show low selectivity for H_2S over CO_2.

The choice of an acid gas treatment process for use in coal conversion plants is influenced by the processes used for subsequent tail gas treating and/or for sulfur recovery. In addition, in the production of high Btu gas, factors such as residual sulfur, CO_2, organics, and moisture levels in the

TABLE 6-1. KEY FEATURES OF SOLVENT PROCESSES USED IN REFINERIES FOR ACID GAS REMOVAL

Process Name	Solvent/Regeant	Operating Pressure (acid gas partial pressure)	Selectivity		Component Distribution*							Solvent Losses (Replacement Requirement)	Utility Requirements†
			H_2S/CO_2	CO_2/HC	COS	CS_2	RSH	NH_3	HCN	Higher Organics	Water Vapor		
PHYSICAL SOLVENTS													
Rectisol	Methanol	High	Good	Poor	a,b	a,b	a,c,d	c,d	a,c,d	a,b,c,d	d	High	Moderate/Low
Selexol	Dimethyl ether of polyethylene glycol	High	Good	Moderate	a,b	a,b	a,c,d	c,d	a,c,d	a,b,c,d	d	Low	Low
Purisol	N-methyl 2-pyrrolidone	High	Good	Moderate	a,b	a,b	a,d	a,d	a,c,d	a,b,c,d	d	Low	Low
Fluor solvent	Propylene carbonate	High	Moderate	Moderate	a,b	a,b	a,d	a,d	a,c,d	a,b,d	d	Low	Low
Estasolvan	Tri-n-butyl phosphate	High	Moderate	Moderate	a,b	a,b	a,d	a,d	a,c,d	a,b,d	d	Low	Low
CHEMICAL SOLVENTS													
Sulfiban	Monoethanolamine (MEA)	Low	Poor	Good	e	e	a,b,d	a,d	e	a,d	d,g	High	Very high
MDEA	Methyl-diethanol-amine	Low	Moderate	Good	a,b	a,b	a,b,d	a,d	e	a,d	d,g	Moderate	High
ADIP	Diisopropanolamine	Low	Poor	Good	a,b	a,b	a,b,d	a,d	e	a,d	d,g	Moderate	High
Fluor Econamine	Diglycolamine (DGA)	Low	Poor	Good	a,b	a,b	a,b,d	a,d	e	a,d	d,g	Low	High
Alkazid	Dimethyl or diethyl glycine	Low	Moderate	Good	f,g	f,g	d,g	a,d	e	a,d	d,g	Low	High
MIXED SOLVENTS													
Sulfinol	Cyclotetramethylene sulfone and diisopropanolamine	Moderate	Poor	Moderate	a,b	a,b	a,b	a,d	a,d	a,b,d	d,g	Low	Moderate
Amisol	Methanol and mono- or diethanolamine	Moderate	Poor	Moderate	a,b	a,b	a,d	a,d	a,d	a,b,d	d,g	High	Moderate

*a) with acid gas stream after simultaneous CO_2 and H_2S removal
b) with CO_2 stream after separate CO_2 and H_2S removal
c) with H_2S stream after separate CO_2 and H_2S removal
d) with aqueous or organic liquid phase prior to or integral with process
e) degrades solvent
f) hydrolyzes
g) remains with treated gas

†Depends on acid gas partial pressure, selective vs. non-selective design, and residual sulfur allowed; rating is for moderate to high pressure application with <10 ppm residual H_2S in treated gas.

treated gas influence the design of methanation and associated guard systems. Based on the published data for various acid gas treatment processes and the results of several other studies evaluating acid gas treatment systems for coal conversion application(19,20,21,31), the following conclusions can be drawn:

- Physical solvent processes are the most likely candidates for use in coal conversion plants where acid gases are at high pressures and selective H_2S removal is desired (e.g., in the Lurgi and Hygas gasification processes). Processes such as Rectisol and Selexol offer high selectivity toward H_2S and would be economical (compared to amine and mixed solvent processes) for high pressure operation. In SNG production, residual sulfur and CO_2 levels obtained are consistent with methanation catalyst protection requirements (i.e., only small sulfur guard beds would be required). Also, water vapor and organics which can deactivate either the sulfur guard or the methanation catalyst are largely removed.

- Amine based processes are not likely to be commercially employed for bulk acid gas removal in SNG production but may be used in conjunction with the production of fuel or synthesis gas. MEA and DEA suffer both excessive degradation and vaporization losses. Even the more stable and less volatile solvents (e.g., DIPA, DGA) are uneconomical at high pressures and are not selective enough toward H_2S. The use of such processes would result in an acid gas stream containing as low as 0.3% H_2S and the remainder CO_2. This presents a major problem for subsequent sulfur recovery/removal. Amine based processes are suitable for nonselective applications to low pressure feed gases such as the low/medium Btu gas from Koppers-Totzek and Wellman-Galusha gasifiers and fuel gas from low pressure liquefaction processes (e.g., COED). One amine solvent (ADIP) has been proposed for use in a commercial SNG facility for the purpose of recovery of hydrocarbons and concentration of H_2S from the concentrated acid gas stream from a physical solvent process (Rectisol).

- Mixed solvents (e.g., Sulfinol) have generally the same advantages and disadvantages as the amine system. Since mixed solvent processes incorporate some of the advantages of the physical solvent, they can be more economical than the amine system for medium pressure application.

Even though all the processes listed in Table 6-1 are reported to have been used in refinery applications, nearly all the data published in the literature on the performance of these systems pertain to applications in natural gas desulfurization. The amine systems are more widely used in refineries than other acid gas treatment systems, primarily because the feed gases are generally at relatively low pressures and temperatures and contain high concentrations of H_2S (high H_2S/CO_2 ratio). In refinery applications, the amine systems can produce a concentrated acid gas suitable as Claus plant feed. As discussed in Section 5.2.1, the product gas in coal conversion processes contains a much lower H_2S level and a much higher level of CO_2 and hence is not suitable for processing by amine systems. Moreover, since amine systems are not suitable for processing hot gases, the product gases from coal conversion require more extensive cooling than when processes such as Selexol are used; such cooling would constitute a thermal penalty. In addition, coal conversion gases contain higher levels of components such as HCN, NH_3, COS and tarry materials which can cause a more rapid degradation of the amine solution. In refinery applications, the amine systems have been shown to be capable of producing a product gas containing a few ppm H_2S and several hundred ppm CO_2 (corresponding to removal efficiencies of more than 99.9% and 99%, respectively).

The Sulfinol and the Selexol processes, which are reported to have been used for the treatment of refinery acid gases, have been used or are planned for use in coal conversion applications. The Sulfinol process has been used at a Koppers-Totzek facility in Turkey. The Synthane pilot plant at Bruceton, Pa., and the Texaco pilot plant at Montebello, Ca., feature Selexol units for the removal of H_2S from product gas. No operating data are currently available on the performance of these processes in either refinery or coal conversion applications.

Although some of the refinery acid gas treatment processes have been used in or would have applications to coal conversion, a number of other processes have been developed or are under development specifically for the treatment of coal conversion acid gases. These processes, which are not discussed in this report, are Rectisol and Benfield solvent processes and hot gas treatment systems using solid sorbents.

6.1.2 Sulfur Recovery

Processing of concentrated sour gases from acid gas treatment units and sour water strippers for the recovery of sulfur in elemental form is widely practiced in refineries using the Claus sulfur recovery process. Sulfur recover from dilute sour gases (less than 10% H_2S) is also practiced in a few refineries using the Stretford sulfur recovery process. Key features of the Claus and Stretford processes are summarized in Table 6-2.

As indicated in Table 6-2, the Claus process is generally applicable to feed streams containing a minimum of 10%-15% H_2S, whereas the Stretford and G-V processes are applicable to feeds containing around 1% H_2S. (Some Claus plants have been designed and are operating on feeds containing as low as 5% H_2S. The Stretford process has also been used with feeds containing more than 10% H_2S. At these high concentration levels, however, the Stretford process is not economically competitive with the Claus process.) The treated gas from the Claus process generally contains several thousand ppm of sulfur compounds (primarily H_2S), whereas the treated gas from Stretford contains less than a few ppm of H_2S. The Claus process is a dry, high temperature process in which H_2S is catalytically reacted with SO_2 (produced by air oxidation of the H_2S) to form elemental sulfur. When processing gases with very high H_2S concentrations (e.g., in most refinery applications), Claus plants are generally designed for "straight through" operation. In this operation mode the entire volume of the gas and a stoichiometric quantity of air to oxidize only one-third of the H_2S to SO_2 are passed through the catalytic reactor. The Stretford is a liquid-phase oxidation system using aqueous solutions of alkaline metavanadate/anthraquinone disulfonic acid. While other reduced forms of sulfur (e.g., CS_2 and COS) are partially removed by the Claus, they are not removed by the Stretford process. Since the Claus process operates at a relatively high temperature, it is also capable of oxidizing some of the hydrocarbons. High concentrations of hydrocarbons, hydrogen cyanide and ammonia (when CO_2 levels are high) can result in Claus catalyst fouling, product sulfur contamination, and equipment corrosion (in the case of HCN).

The Claus process is likely to find wide application for sulfur recovery in coal conversion facilities when selective H_2S removal from gases is practiced. The "split flow" and the "sulfur-burning" designs are likely to be employed for coal conversion applications rather than the "straight through" mode commonly employed in refineries since the high CO_2 levels found in most coal conversion acid gases result in unstable flame conditions in the "straight through" Claus reactor. In the split flow mode, the acid gas stream is divided in the ratio of 2:1 and the smaller stream is oxidized

TABLE 6-2. GENERAL CHARACTERISTICS OF CLAUS AND STRETFORD SULFUR RECOVERY PROCESSES

Process	Process Principle	Limits of Applicability	Control Efficiencies (%)						By-Product	Effect of CO_2	Commercial Applications
			H_2S	COS/CS_2	R-SH	HCN	NH_3	HC			
Claus	Catalytic oxidation of H_2S to elemental sulfur	Straight-through system utilized for higher H_2S concentrations. Split-stream system utilized for lower H_2S concentrations. Minimum of 10-15% sulfur in feed stream.	90 - 95	90	95	Partially oxidized	Partially oxidized	90	Elemental liquid sulfur	Can adversely affect sulfur removal ability and therefore increase plant size. If CO_2 exceeds 30% and NH_3 exceeds 500 ppmv, catalyst plugging problems may occur.	Widely employed in petroleum refinery, natural gas, and by-product coke industry. No known applications to coal gasification.
Stretford	Liquid phase oxidation of H_2S to elemental sulfur in an alkaline solution of metavanadate and anthraquinone disulfonic acid (ADA) salts.	Maximum of 10 to 15% sulfur in feed stream. Present applications are generally for 1% sulfur or less.	99.9 or greater	0	0	-100 (converted to SCN^- in Stretford solution)	0	0	Elemental sulfur	High CO_2 concentrations will decrease absorption efficiency by lowering solution alkalinity. Increasing absorber tower height and base addition are required.	Primarily natural gas service, a few applications to petroleum refining and by-product coke industries. A unit is under construction at the Lurgi gasification facility at Sasol, So. Africa.

with air and recombined with the larger stream to produce elemental sulfur in the catalytic converters. In the "sulfur-burning" mode, liquid sulfur is added to the feed along with air to produce the SO_2 needed for the Claus reaction. Claus plant design and operation in coal conversion applications may require modification to handle high hydrocarbon concentrations in the concentrated acid gas stream resulting from the use of processes such as Rectisol. Alternatively, hydrocarbon removal from Claus feed (and H_2S enrichment) may be accomplished by use of processes such as ADIP. It is likely that overall Claus plant sulfur recovery efficiency will be somewhat lower in coal conversion applications than in refinery applications, primarily because of the less concentrated H_2S feed stream. To minimize catalyst fouling, ammonia and HCN must also be removed from the Claus plant feed. Claus plants have not been used in any of the existing commercial coal conversion facilities but are featured in some of the designs for proposed commercial facilities in the U.S. The Hygas high Btu gasification pilot plant in Chicago reportedly includes a small Claus unit for the treatment of acid gases from a DGA acid gas treatment unit(22). No operational data, however, are available on this unit.

The Stretford process is very likely to be employed for sulfur recovery where (a) low sulfur coals are used as feed in coal conversion facilities, (b) nonselective H_2S removal from gases is practiced, and/or (c) where selective H_2S removal results in the generation of a CO_2-rich stream containing levels of H_2S too large for direct atmospheric discharge. These high CO_2 (and other constituent) levels in coal conversion acid gas streams will necessitate design and operational modifications to those versions of the Stretford process which have been employed in refineries. The modifications include (a) larger towers and more gas/liquid contact surfaces to achieve high H_2S removal efficiencies, (b) caustic addition to maintain proper pH levels, and (c) high rates of solution blowdown to prevent dissolved solids buildup and subsequent precipitation in the system and to maintain solution activity when degradants such as HCN are present in the feed.

6.1.3 Tail Gas Treatment

Depending on the influent gas characteristics and the specific sulfur recovery process employed, the treated gas from a sulfur recovery system may require additional treatment before discharge to the atmosphere. Such additional ("tail gas") treatment may be necessary to achieve a higher level of H_2S removal (e.g., when the Claus process is used for sulfur recovery) and/or for the removal of hydrocarbon and other forms of sulfur (e.g., COS, CS_2, etc.). As with the sulfur recovery processes, the tail gas removal systems have not been used in connection with coal conversion, but many of them are used in refineries (mostly new refineries) to meet air pollution emission regulations.

Table 6-3 summarizes the key features of the sulfur recovery tail gas treatment processes which have been used in refineries. The processes listed in this table fall into three general categories: (a) processes such as IFP-1 and Sulfreen, which are essentially extensions of the Claus process; (b) processes such as Beavon, Cleanair and SCOT, which catalytically reduce the more oxidized sulfur compounds (e.g., SO_2, CS_2, and COS) to hydrogen sulfide which is recycled to the sulfur recovery systems; and (c) processes such as Chiyoda Thoroughbred 101, Wellman-Lord, IFP-2 and Shell CuO, which involve the removal of SO_2 by scrubbing and require feed incineration to convert all sulfur compounds to SO_2.

The first category of processes has been employed exclusively for Claus plant tail gas treatment and is capable of reducing the sulfur level to less than 500 ppmv. As with the Claus process, these processes can tolerate high concentrations of CO_2 in the feed gas. In the Beavon, SCOT and Cleanair processes, hydrogen or synthesis gas is used for the reduction of oxidized sulfur; the reduction is carried out over a cobalt-molybdate catalyst. In existing refinery applications, the product hydrogen sulfide in the tail gas from the Beavon and Cleanair processes is treated for H_2S removal/sulfur recovery by the Stretford process. The alkanolamine process is used for H_2S recovery in the SCOT process. Total sulfur levels of less than 100 ppmv have been achieved by the application of Beavon-Stretford and SCOT-alkanolamine systems (although levels of 250 ppmv are more common). In constrast to the first category of processes (processes which extend the Claus reaction), the reduction processes are adversely affected by high levels of CO_2 in the feed gas. The CO_2 in the feed gas reduces the efficiency of the catalytic reduction of COS and CS_2 and impairs the effectiveness of the Stretford and alkanolamine absorption systems. The third category of processes, which involve incineration

TABLE 6-3. KEY FEATURES OF SULFUR RECOVERY PLANT TAIL GAS TREATMENT PROCESSES

Tail Gas Removal Process	Process Principle	Feed Stream Requirements/ Restrictions	Sorbents/ Solvents	Product	Utility Requirements	COS and CS_2 Removal	Efficiency	Effect of CO_2 in Feed Gas
Chiyoda Thoroughbred 101	Thermal oxidation of sulfur compounds to SO_2, followed by liquid absorption	Incinerated Claus tail gas; no specific requirement on $H_2S:SO_2$ ratio	2% (by wt.) sulfuric acid solution	Gypsum ($CaSO_4 \cdot 2H_2O$) 5 to 20% moisture content	Very high	Largely oxidized by incineration, not absorbed by solution	95% SO_2 or less than 300 ppmv	No effect
Beavon	Catalytic reduction of sulfur compounds to H_2S, followed by Stretford process	Sulfur recovery process tail gas is heated upstream of catalytic reactor; no specific $H_2S:SO_2$ ratio required	Stretford Process solution	Elemental sulfur	Low	Catalytically converted to H_2S	99.8% removal for Claus tail gas containing 4% equivalent H_2S	Reduces conversion efficiency by catalyst; decreases H_2S absorption by Stretford solution
Cleanair	Catalytic reduction of sulfur compounds to H_2S, followed by a continuation of the Claus reaction and Stretford process	$H_2S:SO_2$ ratio can vary up to 8:1 without affecting efficiency; designed specifically for Claus tail gas	Unknown aqueous solution and Stretford process solution	Elemental sulfur	Very low	Catalytically converted to H_2S	Plant effluent normally guaranteed to contain less than 250 to 300 ppm SO_2 equivalent	Reduces conversion efficiency of catalyst; decreases H_2S absorption by Stretford solution
IFP-1	Liquid phase continuation of Claus reaction at a low temperature	$H_2S:SO_2$ ratio maintained in the range of 2.0 to 2.4	Polyalkaline glycol	Elemental liquid sulfur	Very low	Not removed in catalytic reactor	Capable of reducing sulfur species in Claus tail gas to 2000 ppm as SO_2	No effect
IFP-2	Incineration of tail gas followed by ammonia scrubbing. Solution is evaporated to produce a concentrated SO_2 stream which is returned to the Claus plant.	$H_2S:SO_2$ ratio maintained in the range of 2.0 to 2.4	Aqueous ammonia solution	Elemental liquid sulfur	High	Oxidized by incineration, not removed in catalytic reactor	Capable of reducing sulfur species in Claus tail gas to less than 500 ppm	No effect

(continued)

TABLE 6-3. CONTINUED

Tail Gas Removal Process	Process Principle	Feed Stream Requirements/ Restrictions	Sorbents/ Solvents	Product	Utility Requirements	COS and CS_2 Removal	Efficiency	Effect of CO_2 in Feed Gas
Sulfreen	Solid phase continuation of Claus reaction at a low temperature	Optimum performance requires H_2S:SO_2 ratio of 2:1	None; sulfur vapor condensation process utilized	Elemental liquid sulfur	Very low	Not appreciably removed	Capable of removing 80 to 85% of sulfur in the tail gas	No effect
Shell Copper Oxide	Thermal oxidation of sulfur compounds to SO_2, followed by adsorption by CuO; a concentrated SO_2 stream is produced by desorption with a reducing gas (H_2)	Incinerated Claus tail gas; no specific requirement on H_2S:SO_2 ratio	Copper oxide	Concentrated SO_2 stream	No data available	Oxidized by incineration	90% SO_2 removal	?
Wellman-Lord	Thermal oxidation of sulfur compounds to SO_2, followed by liquid absorption; concentrated SO_2 is produced and recycled to Claus plant	Incinerated Claus tail gas; process can handle SO_2 concentrations well over 10,000 ppm	Concentrated sodium sulfite, bisulfite solution	Concentrated SO_2 stream (up to 90% SO_2 content)	High	Oxidized by incineration, not removed by process	Can remove in excess of 95% of SO_2	No effect
SCOT	Sulfur species are catalytically reduced to H_2S; H_2S is scrubbed in a regenerable amine system	Applicable to Claus tail gas	Alkanolamine solution	Concentrated H_2S stream	Moderate	Catalytically reduced to H_2S	Can remove 97% of sulfur species	Reduces conversion efficiency by catalyst; high CO_2 levels reduce efficiency of alkanolamine system

followed by SO_2 recovery, has been applied to Claus plant tail gas and to utility boiler flue gases. These processes are capable of removing over 90% of the total sulfur in the feed gas. The Chiyoda Thoroughbred 101 and the Shell-CuO processes which employ sulfuric acid and CuO as sorbents, respectively, are not affected by high levels of CO_2 in the feed gas. In the Wellman-Lord process the sorbent is an alkaline solution of sodium sulfite/bisulfite whose capacity for SO_2 absorption may be affected by very high levels of CO_2 in the feed gas. (Use of the Wellman-Lord process for SO_2 removal has been successfully demonstrated on flue gases from coal-fired utility boilers which would contain over 10% v CO_2.)

With the exception of the catalytic reduction processes (Beavon, Cleanair and SCOT) which may not perform well on high CO_2 tail gases,* all of the processes listed in Table 6-3 are likely candidates for Claus plant tail gas desulfurization in coal conversion facilities. The processes which remove sulfur as SO_2 require incineration of the tail gas to convert sulfur compounds to SO_2. Use of these systems in an integrated commercial coal conversion plant would be attractive if desulfurization of boiler flue gases is also required since the desulfurization can possibly be combined in a single operation. It may also be possible to treat the gases separately for SO_2 absorption, but regenerate SO_2-rich absorbents in a single unit. The choice of individual processes will be dictated by overall economics and specific emission limitations at the plant site.

6.1.4 Incineration (Flaring) of Waste Gases

Flaring of waste gases is commonly practiced in refineries as a safety and emission control technique. The primary purpose of flaring is to convert organics, carbon monoxide, and reduced sulfur and nitrogen compounds to less hazardous forms (e.g., CO_2, SO_2, NO_x). Most flares in refinery service are elevated above ground level to provide for improved pollutant and heat dispersion. Steam (or other inert gas) is injected in the combustion zone of the flare to enhance turbulent mixing of waste gas and air and to suppress smoke formation. Since the quantity and composition of refinery waste gases vary widely over short periods of time, modern flares incorporate sensors and feedback controls to regulate air and steam feed rates in response to changing waste gas combustion characteristics.

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*Union Oil Co., the vendor-licensor of the Beavon process, however, intends to offer a 250-ppmv performance guarantee for the process in coal gasification applications(23).

Because of the highly variable nature of waste gases commonly flared, it is generally difficult to achieve the proper combustion conditions consistent with minimum emissions of oxidizable substances. Thus, even with sophisticated flare control systems, emissions of CO, unburned hydrocarbons, and odors are generally higher from flares than from other stationary combustion sources of a comparable heat rating. Although some noise is inherent in the release of steam through flare orifices, the venting of combustion products to the atmosphere, and the combustion process itself, such noise can be minimized by proper flare design (e.g., reducing the size of steam injection orifices) and operating conditions (e.g., using a minimum amount of smoke suppressant).

Waste gases in coal conversion facilities which would be treated by flaring are primarily those associated with transient operations. Such waste gases would be highly variable in composition and quantity and hence a high degree of combustion control is needed for effective emission control.

6.1.5 Control of Fugitive Emissions and Odors

Fugitive hydrocarbon emissions can be a major source of air pollution in petroleum refineries. Major sources of such emissions which would have counterparts in coal conversion plants inlcude storage vessels, loading and transportation, pump and compressor seals, pressure relief valves, pipeline valves and flanges, pipeline blind changing and sampling lines. In new plants many of these emissions can be significantly reduced by proper design and equipment selection. For example, highly volatile products such as butane and naphtha must be stored in pressure tanks; less volatile materials such as kerosene and crude oil can be stored in floating-roof and variable vapor space tanks. It has been shown that centrifugal pumps with mechanical seals have approximately 33% lower hydrocarbon emissions than centrifugal pumps with packed seals(24). Fugitive emissions caused by leaks from pumps, valves, etc. can be minimized through routine equipment maintenance. Although these control methods are not unique to refineries, the extent of control required would depend on the number of sources and magnitude of emissions which would vary from industry to industry and from plant to plant depending on the size of the operation, process employed, materials handled, age of the equipment and maintenance programs. In comparison to refineries, most coal conversion plants are expected to have a more restricted range of liquid and gaseous products and on an equivalent product basis fewer sources of fugitive emissions. Furthermore, coal-derived liquids would have less of the more volatile compounds than crude oil and petroleum-derived products (e.g., syncrude vs. crude oil).

The refinery add-on fugitive hydrocarbon emission control methods which may be applicable to coal conversion include use of refrigeration and scrubbing vapor recovery systems on storage tanks, and disposal of collected hydrocarbon vapors by thermal or catalytic incineration.

As in refineries, production of odorous compounds (e.g., H_2S, NH_3) would be associated with the operation of almost all coal conversion plants. Because of the highly odorous nature of some of these compounds (e.g., mercaptans and heterocyclic aromatics such as pyridine and thiophene), their release to the atmosphere, even in very small quantities, can present significant odor problems. As with the hydrocarbon emissions, options for the control of odor are limited to source control, incineration and carbon adsorption. Since in an integrated facility fugitive emissions (e.g., from spills and leaks) and emissions from nonprocess sources (e.g., cooling towers and wastewater treatment units) can contribute significantly to the total odor emissions, good housekeeping practices, proper operating procedures and routine maintenance are essential to minimize the odor problem.

6.2 AQUEOUS WASTE PROCESSING AND WATER POLLUTION CONTROL

The major refinery aqueous waste treatment processes which may be applicable (in some cases with certain design and operational modifications) to coal conversion waste streams are sour water stripping for hydrogen sulfide and ammonia removal; gravity separation, flotation and emulsion breaking for the removal of oil from oily and tarry wastewaters; lagooning, biological treatment, chemical oxidation and carbon adsorption for the removal of organics; and thickening, centrifugation, filtration, and drying for sludge dewatering.

6.2.1 Sour Water Stripping

Stripping is widely used in petroleum refineries for the removal of dissolved gases (primarily H_2S and NH_3) from sour waters. Stripping enables recovery of valuable products (ammonia and hydrogen sulfide) and significantly reduces the waste loading on downstream treatment units. Stripping of dissolved gases can be effected by contacting the wastewater with a stripping medium such as steam, flue gas, nitrogen, air, and carbon dioxide. The most common stripping medium in refineries is steam, and the stripping operation is usually conducted in a tower (packed or trays) with countercurrent (steam up, water down) flow pattern. Acid (for H_2S removal) or alkali (for NH_3 removal) may be added to the raw wastewater to improve stripping efficiency. Depending on the H_2S and NH_3 concentrations of the overhead vapors, the stripped gases are sent to an acid gas treatment unit for further concentration before sulfur recovery; processed directly for recovery of sulfur (e.g., in a Claus plant), sulfuric acid, anhydrous or aqueous ammonia or ammonium sulfate; or disposed of by flaring. The flaring of stripper off-gases is generally being phased out due to SO_2 and NO_x emission limitations.

Conventional steam stripping of the refinery sour waters can achieve greater than 99% removal of H_2S, and up to 95% removal of NH_3. Since low molecular weight phenols are somewhat volatile, sour water stripping can also result in the partial removal of phenols (up to 90% in refinery applications(25).

One major problem with conventional steam stripping is the difficulty in recovering ammonia. One patented application of steam stripping which generates separate concentrated H_2S and NH_3 streams and has been used recently in refineries is the Chevron WWT process(26). In the Chevron process separate towers, which operate under different pressures and temperatures, are used for H_2S and NH_3 stripping. Since the product ammonia stream contains some residual H_2S, this stream is scrubbed with liquid ammonia prior to processing to convert the gaseous ammonia to anhydrous or aqueous ammonia or to ammonium sulfate. The treated wastewaters from the Chevron process can have residual H_2S and ammonia as low as 5 and 50 mg/l, respectively.

The coal conversion wastes which would contain high levels of H_2S and NH_3, and hence would be treatable by stripping, include raw gas quench waters and particulate scrubber waters from gasification, waste liquor purge from liquefaction, separated waters from hydrotreating, and condensates generated in hydrogen production units. Some of these streams contain smaller quantities of hydrogen cyanide and carbonyl sulfide which, because of their volatility, would also be partially or totally removed by stripping. The fate of these compounds depends upon the subsequent processing of the stripper off-gas. When the off-gas is incinerated, these substances are expected to be largely destroyed. When acid gas treatment is employed, these substances may be destroyed (e.g., in the Benfield process) or may become components of the concentrated acid gas stream, the treated gas stream or the process solvent. In the treatment of the concentrated acid gas stream (or the stripper off-gas) for sulfur recovery, HCN is largely destroyed while carbonyl sulfide is partially destroyed (e.g., in the Claus process) or unaffected (e.g., in the Stretford process).

Neither the Chevron process nor conventional stripping has been employed at pilot coal conversion facilities in the U.S. to date. Conventional steam stripping with ammonium sulfate recovery, however, has been used at the Sasol coal conversion complex in South Africa. A recent engineering study by C. F. Braun and Company comparing various stripping processes for application to coal gasification indicate that the Chevron process has higher capital and operating costs than conventional steam stripping without by-product recovery(27). The value of recovered ammonia, however, significantly offsets the added cost.

6.2.2 Oil and Suspended Solids Removal

In refineries, gravity separation is usually the first step in the treatment of oily wastewaters for the removal of bulk separable oil and suspended solids. API separators, which are gravity separators designed in accordance with the criteria suggested by the American Petroleum Institute (API), are widely used in petroleum refineries for this purpose(12). Gravity separation is also used following biological or chemical treatment for the removal of biological and chemical flocs. In gravity separation the wastewater is allowed to undergo "quiescent settling" in a basin. The oil globules, which are lighter than water, float to and are collected at the surface; the settleable solids settle to the bottom and are recovered as sludge. The settling basins are usually rectangular or circular in shape with "accessories" for the introduction of raw wastewater and collection of effluent, sludge and/or oil. To maximize space utilization, the settling basin design may incorporate use of inclined parallel plates/tubes, each representing a "mini basin" within which solid-liquid separation takes place. The efficiency of gravity separation depends on the wastewater characteristics and the hydraulic ("surface area") loading of the basin. The following ranges of removal efficiencies have been reported for the API separators in refinery oil-water separation applications: 10%-50% suspended solids; 50%-99% free oil, 5%-35% BOD and 5%-30% COD.

Although also applicable to and used for the separation of solids heavier than water, dissolved flotation is most widely used in lieu of or as a supplement to conventional gravity separation for the removal of separable oils from oily wastewaters. Air is dissolved under pressure in a portion of the raw or treated wastewater or in the entire volume of the raw wastewater. In all cases, the total wastewater volume is subsequently discharged to an open basin (the flotation basin) where minute air bubbles which are released attach themselves to the oil particles and float them to the surface at a faster rise rate than would be achieved otherwise. The reported data for refinery applications indicate that without the addition of chemicals, flotation can result in 70%-90% removal of separable oils, 5%-25% BOD removal, 5%-20% COD removal and 10%-40% suspended solids removal(28). In designs for the gasification of coal using the Lurgi process, the tar/oil separator operates on the flotation principle.

Chemicals such as iron and aluminum salts and polymeric organics are often added as coagulants or coagulant aids to improve the efficiency of gravity separation and flotation operations. When added to wastewaters, these chemicals can destabilize colloidal particles and agglomerate fine particles into larger flocs which settle or rise at a faster rate. Particle growth is often facilitated by gentle mechanical mixing (flocculation). When used in conjunction with API separators or air flotation units, coagulation/flocculation can increase removal efficiencies and/or enable higher throughput rates.

When very high levels of oil and suspended solids removal are desired (e.g., for certain reuse applications), the conventional treatment such as gravity separation and chemical treatment may be followed by filtration through a bed of inert solids such as sand, diatomaceous earth or anthracite. The suspended solids trapped in the filter are periodically removed through filter backwashing. As a polishing step for the API separator effluent, sand filtration has been reported to achieve the following removal efficiencies: 70%-75% suspended solids, 52%-83% free oil, 25%-44% COD and 36% BOD(12).

Gravity separation and flotation would probably be the most suitable first step for the treatment of oily wastewaters and wastewaters containing settleable solids in coal conversion plants. As discussed in Section 5.3, such wastewaters include raw gas quench waters and waste liquor purge from product liquids separation. Depending on the availability, cost and the quality of the plant raw water and the effluent discharge requirements, the wastewater treatment system for integrated coal conversion facility may incorporate chemical coagulation and/or filtration of the API separator effluent or the effluent from biological wastewater treatment units to produce an effluent water suitable for recycling. The design of the API separator, flotation units and chemical coagulation and filtration operations should be tailored to the particular wastewaters which are to be treated. The design of full scale units should be based on the criteria (e.g., surface area loading for gravity separation units, air-to-solids ratio for flotation and hydraulic loading and backwash requirements for the filtration units) developed in bench/pilot scale tests, using actual coal conversion wastewaters or wastewaters having compositions approximating those anticipated from a given coal conversion design.

The wastewater treatment at the Sasol, South Africa, coal conversion plant uses (a) API separators for the treatment of the gas reforming plant condensate; (b) Lurgi process tar/oil separators which operate on the flotation principle; (c) flocculation of oily wastewaters from the Fisher-Tropsch oil production and refining units; and (d) sand filtration for the treatment of the trickling filter effluent(29). No data are currently available on the composition of the wastewater handled at the Sasol plant and the performance of the treatment units. The designs of high Btu gasification plants which have been proposed for the U.S. incorporate gravity settling of ash quench water (in the El Paso Burnham, New Mexico and ANG, North Dakota plants), API separation for the raw gas quench water and air flotation of the API separator effluent (in the Wesco, New Mexico plant)(30,31,32).

6.2.3 Dissolved/Particulate Organics Removal by Biological Oxidation

Following the removal of bulk H_2S and NH_3 from sour waters by stripping and the removal of oil and settleable solids from oily and other process wastewaters by gravity separation and flotation, in most large refineries the combined plant effluent is treated by biological oxidation before discharge into natural waters or municipal sewers or reuse. In biological treatment, the dissolved and/or collodial organics are converted to inorganic end products and microbial cells by the action of microorganisms. The resulting biomass (sludge) is subsequently removed by gravity separation. Although biological oxidation can be conducted under anaerobic (in the absence of oxygen) conditions, aerobic (in the presence of oxygen) treatment is preferred for most applications because of the high efficiency and lower costs. Anaerobic treatment is usually used for concentrated organic wastewaters and sludges.

Table 6-4 lists the most commonly used biological treatment systems including reported efficiency ranges for the removal of BOD, COD, SS, oil, phenols and sulfide in applications to refinery wastewaters. As noted in the table, biological treatment can result in up to 90% removal of the biologically oxidizable compounds.

TABLE 6-4. EFFICIENCY OF BIOLOGICAL TREATMENT FOR PETROLEUM REFINERY EFFLUENTS*

Biological Treatment Method	Parameters† (% Removal)					
	BOD	COD	SS	Oil	Phenols	$S^=$
Activated sludge	88-90	60-85	-	-	95-99+	97-100
Trickling filters	60-85	30-70	50-80	50-80	-	-
Waste stabilization pond (aerobic)	40-95	30-65	20-70	50-90	-	-
Aerated lagoon	75-95	60-85	40-65	70-90	90-99	95-100
Cooling tower oxidation (air stripping)	90+	90+	-	-	99.9	-
Spray irrigation	99+	90+	99+	70-90	99.9	99+

*The ranges of values reflect differences in wastewater characteristics and system design and operating conditions.

†Thiocyanates are approximately 70% removed by these processes.

Evaporation and retention ponds are widely used in the petroleum industry for ultimate disposal of raw or treated wastewaters, as tertiary treatment basins following biological treatment or as temporary storage ponds for controlled effluent discharge. Although not classified strictly as waste stabilization ponds, these ponds do achieve some biodegradation of organics. These ponds, which are also referred to as "holding basins," "lagoons," "oxidation ponds," "settling basins," etc., are usually natural or man-made earthen reservoirs into which wastewaters are discharged. These ponds may be lined with impermeable materials (plastic, clay, asphalt, etc.) to prevent infiltration. The retention of the wastewater in the pond provides for natural evaporation, settling of solids, biological decomposition of organics and loss of the more volatile components of the waste to the atmosphere. In geographic regions where annual evaporation exceeds precipitation, the ponds are generally designed to have no effluent discharge. Ponds can also be used for temporary waste storage and controlled discharge during high flows in the receiving waters. Evaporation/retention ponds require minimum maintenance and, when large land areas are available, can be the most economical method for wastewater disposal. The Sasol gasification complex in South Africa uses a settling pond for polishing treatment of the total plant effluent before discharge into a river. Settling ponds are also used at all U.S. coal conversion pilot plants and have been featured in all proposed designs for commercial SNG facilities in the U.S.

The use of pure oxygen (in place of air) in the biological treatment of wastewaters by the activated sludge process has received considerable attention in recent years and a number of pure oxygen activated sludge plants are currently in operation handling municipal sewage and a variety of industrial wastewaters. Compared to a conventional air activated sludge process, the pure oxygen process is claimed to have several advantages, including higher efficiency and loading rate, less sludge production, superior characteristics of the sludge, and lower overall costs. In coal conversion facilities which employ on-site oxygen production for process use (e.g., for high Btu gasification using processes such as Lurgi), the use of an oxygen activated sludge process would be attractive since a source of oxygen would be available for wastewater treatment.

Although not specifically used for biological wastewater treatment, cooling towers have been used at several refineries for biological treatment of selected waste streams. The use of cooling towers for biological treatment has also been demonstrated at the Sasol, South Africa, gasification plant. Cooling towers provide ideal temperatures and surfaces for biological activity. The oxygen required by microorganisms is provided by the extensive aeration which accompanies the cooling process. In refinery applications, phenolic wastewaters have been used as cooling water make-up and more than 99% destruction of phenols has been reported(12). In a demonstration program at the Sasol plant, the ammonia stripper bottoms have been used as cooling tower make-up(33). In this program the bioactivity, foaming, fouling and corrosion which may be expected from the use of this wastewater for cooling water make-up have been evaluated and the results have been used as a basis for the design of a cooling/oxidation tower system for the proposed El Paso Burnham plant in New Mexico.

Where soil, climate and hydrological conditions are favorable, biological treatment may also be accomplished by the application of partially treated wastewaters to soils. Microbiological processes in the soil can result in the degradation of most biodegradable organics and the oxidation of ammonia, sulfide, and other pollutants. In addition, physical adsorption and filtration results in the removal of phosphorus and most metalic elements. Depending on the particular soil, the geographic location, and the rate of wastewater application, net runoff or percolation may or may not be generated. Continued application of wastewaters containing high levels of dissolved solids to soils can result in salinity and/or alkalinity buildup to the point of adversely affecting plant growth. The accumulation of certain trace elements and organics in soils may also present toxicity problems for plants or herbivores. When improperly sited, designed and oeprated, land application of wastewaters may present odor problems or result in the contamination of surface waters and groundwaters.

In comparison to chemical and physical treatment processes (e.g., activated carbon adsorption, stripping, etc.), biological processes are significantly more sensitive to wide fluctuations in wastewater characteristics. When such fluctuations are anticipated (e.g., discharge from batch and transient operations), the biological treatment should be preceded by storage/mixing facilities for equalization of flow and strength. Certain biological treatment processes, such as the waste stabilization pond, aerated lagoon, and completely mixed activated sludge process, can tolerate limited and short duration variations in wastewater characteristics since they feature near complete mixing and large volume and retention time. Nutrients such as nitrogen (N) and phosphorus (P) compounds are necessary for microbiological growth. A BOD:N:P ratio of approximately 100:5:1 is generally necessary for the biological treatment of most industrial wastewaters. When a wastewater is deficient in nutrients, they must be added to the raw wastewater prior to biological treatment. Coal conversion wastewaters are expected to have a sufficient amount of nitrogen (in the form of ammonia) but be deficient in phosphorus content. At the Sasol plant, South Africa, which uses trickling filtration for biological wastewater treatment, phosphate is added to the raw wastewater to allow efficient operation.

In a coal conversion plant, biological oxidation would most likely be used after the bulk of organics, reduced inorganics (e.g., H_2S, NH_3) and particulate matter have been removed by processes such as gravity separation, coagulation/flocculation, flotation, phenosolvan and stripping. Several factors affect the applicability and performance of biological oxidation for the processing of coal conversion wastewaters. These factors relate to wastewater constituent biodegradability, toxicity, pH, nutrient content and fluctuations in characteristics. In contrast to the organics in refinery wastewaters which are primarily aliphatic and mostly biodegradable, the organics in coal conversion wastewaters tend to be highly aromatic. While certain aromatic compounds such as simple phenols are readily degradable (at relatively dilute levels), the more complex and substituted phenols, polycyclic hydrocarbons and heterocyclic organics are generally less readily degradable or essentially nonbiodegradable (e.g., pyridine). Some of the organics (e.g., phenols at high concentration levels), trace elements (e.g., arsenic and mercury) and inorganic anions (e.g., cyanide and thiocyanate) can be toxic to microorganisms at high concentration levels. Biological processes are generally most efficient when the pH of the wastewater is in the 6-8 range. The pH of the wastewater also affects toxicity of certain wastewater constituents. For example, the toxicity of sulfide increases with decreasing pH. Provided that adequate nutrients are added, the wastewater pH is maintained near optimum and the wide fluctuations in raw wastewater characteristics are prevented, coal conversion wastewaters should be treatable by biological means either alone or in combination with sanitary sewage.

As noted above, the Sasol plant in South Africa employs trickling filters for the treatment of combined plant and municipal wastewater. Oxidation towers are featured in the proposed designs for the El Paso Burnham and Wesco SNG plants in New Mexico for the treatment of ammonia stripper bottoms and biological treatment effluent, respectively. An oxidation tower is also proposed for the ANG (North Dakota) SNG plant for the treatment of stripped gas liquor. Since no commercial coal liquefaction or high Btu coal gasification facility currently exists in the U.S. and very little data are available on wastewater characteristics and efficiency of treatment processes at foreign facilities (in terms of concentrations of specific pollutants in the influents and effluents of biological treatment units), the optimum design criteria and operating conditions for the biotreatment of coal conversion wastes cannot be defined at this time. Several studies (34-37) are currently under way which are aimed at the characterization of coal conversion wastewaters and evaluation of the biotreatability of such wastes.

6.2.4 Dissolved Organics Removal by Activated Carbon Adsorption

Several refineries have installed activated carbon adsorption systems for the treatment of effluents from biological treatment or API separator. Activated carbon (in granular and powdered form) has also been used for the treatment of municipal and a variety of industrial wastewaters. In comparison to biological processes, carbon adsorption is unaffected by the presence of toxic constituents in the wastewater and the fluctuations in wastewater characteristics.* Granular carbon is used in fixed or moving columnar beds with either upward or downward wastewater flow. Powdered carbon is generally mixed with the wastewater and is subsequently removed by flocculation and/or filtration.

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*When granular carbon is used in beds, some biological growth becomes established in the bed which contributes to the overall organic removal efficiency (via biodegradation). In this case the treatment efficiency would be affected by the presence of toxic chemicals or by wide fluctuations in wastewater characteristics.

Because of its relatively high cost, the use of activated carbon adsorption for wastewater treatment would generally be limited to (a) removal of residual organics from the biological treatment effluents, when such removal is necessary; (b) treatment of wastewaters containing high levels of refractory organics or toxic chemicals; (c) in combination with chemical coagulation and filtration in a "physical-chemical" combination treatment scheme in lieu of biological treatment; and (d) recovery of by-products (e.g., phenols) from the wastewaters. Except when used for by-product recovery (e.g., for the recovery of phenols from dilute wastewaters), the spent carbon is usually regenerated by thermal treatment. In polishing of biologically treated refinery wastes, removal efficiencies of up to 75% COD, 77% TOC and over 99% phenols have been reported for granular carbon adsorption(38).

The use of activated carbon adsorption in commercial coal conversion facilities would probably be limited to effluent polishing for water reuse or discharge into receiving waters. Because of the relatively high cost of activated carbon adsorption and the availability of alternative treatment/disposal methods, the proposed commercial coal conversion plants for the U.S. do not incorporate use of activated carbon adsorption. Because of the land availability and the goal of attaining zero discharge, the proposed plants are to use evaporation ponds (supplemented by distillation using process heat) for ultimate wastewater disposal or water recovery. Due to the differences in the characteristics of the coal conversion and refinery wastewaters (specifically with regards to the types of organics present), the performance of carbon adsorption in treating coal conversion wastewaters cannot be accurately determined based on the performance data reported for refinery waste treatment. In general, for any type of wastewater, the efficiency of activated carbon adsorption, the most suitable type of carbon, and the criteria for the design of large scale units are determined through laboratory adsorption isotherm tests and laboratory/bench-scale column experiments. In certain coal conversion processes (e.g., Synthane and COED) the use of carbon adsorption is attractive because a char which is produced may have some capacity for sorption of organics. Studies by DOE-PERC have indicated that the Synthane char has adsorptive properties similar to those of commercial activated carbon(35). Even though the char may have a much lower adsorption capacity than activated carbon, it may provide an economical source of carbon for wastewater treatment at coal conversion plants. The spent char would be combusted/gasified in the normal manner.

6.2.5 Chemical Oxidation of Organics and Reduced Inorganics

Chemical oxidation processes using oxidants such as oxygen (air), ozone and compounds of chlorine have been used in industry for the treatment of cyanide, sulfide, phenolic and thiocyanate wastes or their conversion into biologically degradable substances. Air oxidation of foul waters having a high sulfide content and spent caustic solution is being practiced at several refineries using patented processes (e.g., Sulfox Process). In these cases the wastewaters do not contain economically recoverable quantities of ammonia or H_2S to justify treatment by stripping with subsequent by-product recovery. Air and steam (for temperature control) are mixed with the wastewater under pressure and the wastewater is passed through a sulfide oxidation column which provides the necessary contact time for oxidation. Air oxidation results in the conversion of sulfide to thiosulfate and partial conversion of thiosulfate to sulfate. Air oxidation thus lowers the oxygen demand of the sour water for subsequent biological oxidation or discharge to receiving waters. Air oxidation would probably be inapplicable to the treatment of coal conversion sour waters because many of such wastewaters contain relatively large quantities of ammonia which can be recovered as a valuable by-product. Furthermore, when ammoniacal sour waters are treated by air oxidation, the ammonia would be released in the column off-gases and may present an air pollution problem. In addition, the oxidation of sulfides to thiosulfate and sulfate may be undesirable since it increases the total dissolved solids in the wastewater, thus prohibiting further uses of water for certain purposes.

Ozone has been reportedly applied in the treatment of refinery wastewaters as a cleanup step following biological oxidation and sedimentation. Reductions in phenol concentrations from 0.16-0.4 mg/l to less than 0.003 mg/l have been reported(12). Under proper conditions, ozonization should be effective in destroying most biologically refractory organics, including many of those present in coal conversion wastewaters. Bench scale ozone treatment of Synthane raw gas quench condensate indicates that complex organics (e.g., quinolines and indanols) and inorganics (e.g., SCN^-) can be largely removed with adequate ozone dosage(39). Because of the high cost of ozonization (compared to other residual organic removal techniques such as carbon adsorption and oxidation with chlorine compounds), the application of ozonization to coal conversion wastes would probably be limited to polishing treatment to meet effluent discharge requirements or for reuse.

6.2.6 Treatment of Slop Oil and Sludges

Slop oil (i.e., the oil separated from wastewaters by gravity separation and flotation) still contains a large amount of water (mostly in emulsified form) which may require removal prior to incineration or processing for oil recovery. Emulsions can be "broken" by a number of methods including heat treatment with or without chemical addition, precoat filtration, distillation, centrifugation and electrolytic coagulation. It is expected that some of these methods, particularly heat treatment and distillation, will find application in commercial coal conversion facilities for the treatment of tars and oils removed from raw gas quench waters.

Sludges generated as a result of physical, chemical or biological treatment require further treatment for concentration and volume reduction (dewatering) prior to disposal. Sludge dewatering is necessary to enable economical land disposal or incineration. Sludge concentration methods which have been used in refineries include gravity thickening, centrifugation, vacuum filtration, filter presses, and use of drying beds. These methods have also been widely used in municipal and other industrial wastewater treatment practice and considerable experience with them is available in a variety of applications. Table 6-5 presents reported data on solids concentration levels obtained by use of various sludge concentrating processes handling chemical and biological sludges. Chemicals such as lime, ferric salts and synthetic organic polymers may be added to sludges to improve dewaterability. In general, biological sludges tend to be more difficult to dewater than inorganic sludges. Biological sludges and some concentrated organic wastes can also be further concentrated by use of anaerobic digestion whereby a portion of the organic material is converted to methane and carbon dioxide. In addition to the reduction in sludge volume, anaerobic digestion improves sludge dewaterability and filterability.

TABLE 6-5. SOLIDS CONCENTRATION OBTAINED BY VARIOUS SLUDGE CONCENTRATING PROCESSES*

Process	Type of Sludge Processed	Solids Concentration Obtained (%)
Gravity thickening	Activated sludge	5-8
Centrifugation	Activated sludge	6-10
	Lime softening sludge	53-57
Vacuum filtration	Activated sludge	15-20
Drying beds	Primary and activated	~40†

*The ranges of values reflect differences in sludge properties, system design and operating conditions.
†After 15 days of drying, for one specific application.

The efficiency and cost of sludge concentration and dewatering are determined primarily by such sludge characteristics as concentration, size, shape and chemical composition of solids and by viscosity and chemical composition of the sludge liquid. For application to sludges for which previous experience does not exist, the criteria for the design of full scale units and the determination of the optimum operating conditions are usually determined by laboratory experiments and bench-scale studies (e.g., column settling tests for gravity thickening and "leaf" filter tests for vacuum filtration).

Sludges in coal conversion plants which may require thickening and dewatering prior to ultimate disposal include ash quench sludges, sludges from air pollution control systems and chemical and biosludges from wastewater treatment. Based on expected gross similarities between these sludges and the sludges encountered in refineries and in the treatment of municipal and other industrial wastewaters, conventional sludge thickening and dewatering methods such as gravity thickening, centrifugation, vacuum filtration and drying beds should be applicable to the processing of coal conversion sludges. Since no integrated commercial coal conversion facility currently exists in the U.S. and no data are available on the characteristics of the sludges from commercial coal conversion facilities abroad, the preferred process and the optimum operating conditions for the treatment of coal conversion sludges cannot be determined at this time. Because significant variations in sludge characteristics are expected from plant to plant (reflecting differences in the type of coal processed; coal conversion, product purification and upgrading operations used; and the air and water pollution control processes employed), the selection of the optimum sludge processing method should be on a case-by-case basis. The Sasol coal conversion plant in South Africa uses gravity thickening for concentration of ash quench sludge, anaerobic digestion for conditioning of biosludges from trickling filter units and drying beds for the ultimate disposal of the anaerobically digested sludge. Detailed sludge characteristics data and performance information are not available for the operation at Sasol. The raw wastewater handled at the Sasol plant is a combination of municipal and coal conversion plant wastes and hence the sludges would be expected to be different from those for a plant handling solely coal conversion wastes.

6.2.7 Approaches to Waste Volume and Strength Reduction

Several approaches are used in petroleum refineries for wastewater volume and strength reduction. These approaches, which include or provide for wastewater segregation, by-product recovery, water reuse and recycling and good housekeeping practices can also be incorporated in the design and operation of integrated commercial coal conversion facilities to lower wastewater treatment requirements and costs.

Most refineries use a system of segregated sewers for separate collection, transportation and treatment of sour waters, oily waters, relatively "clean" process waters and storm runoff. Such separation of dilute and concentrated wastewaters and wastewaters of significantly different composition provides for more effective and economical treatment of the separated streams (e.g., steam stripping of the sour waters and removal of oil from oily waters), recovery of valuable by-products (e.g., recovery of phenols from spent caustic solutions), and water reuse/recycle (e.g., use of sour water stripper bottoms as the make-up water for cooling towers).

Wastewater segregation systems similar to those used in refineries are used in existing coal conversion plants abroad and are included in the designs for the proposed high Btu commercial gasification facilities in the U.S. The system for the proposed Burnham (New Mexico) SNG facility, for example, allows for the separation and separate treatment of the following streams: tar-rich aqueous condensates, oil-rich aqueous condensates, methanation condensate, and raw water treatment brines, sludges and ash quench water. The segregation of condensates containing large quantities of organics from other wastewaters in a coal conversion plant is especially important in those facilities which use processes such as Lurgi, H-coal, COED, Synthoil, etc. which generate significant quantities of tars and oils. In these facilities, the waste separation enables recovery of tars and oils from relatively small wastewater volumes and reduces the load on the downstream processing units. The separated tars and oils may be incinerated on-site as fuel, injected into the gasifier/pyrolysis units, used for briquetting of coal fines, or sold for chemical recovery or fuel use. In many Lurgi facilities, wastewater treatment for tar/oil removal is followed by the use of the Phenosolvan process for the recovery of crude phenols. Recovery of phenol as a by-product would also be applicable to raw gas quench condensate in other gasification and liquefaction processes (e.g., Hygas, COED) which generate significant quantities of phenols. The recovery of tars, oils and phenols from condensates generates an effluent which can be steam stripped, alone or in combination with other plant sour waters, for the recovery of NH_3 and H_2S. Another example of by-product recovery at a gasification plant which would be possible through waste segregation and separate treatment is the recovery of char fines from raw gas quench condensates (e.g., in the CO_2-Acceptor process) and/or cyclone slurries (e.g., in the Hygas process) via settling and dewatering.

Examples of water reuse/recycling possibilities in an integrated commerical coal conversion plant include the use of boiler blowdown steam and knockout drum condensates and ammonia stripper bottoms as cooling water makeup; use of clean condensates (e.g., methanation condensate in high Btu gas production) for boiler feed waters; use of cooling tower blowdown and raw water softening brines as ash quench water makeup; recycling of the settled raw gas quench water to the quench tower; recycling of the settled ash quench water to the wash transport system; and treatment of waste brine by distillation and use of distillate as boiler feed water. To minimize water wastage and wastewater generation, it is essential that good housekeeping and water conservation measures be incorporated in the design of integrated facilities and be observed during the operation of such plants. Such measures may include elimination of leaks, routine equipment maintenance and personnel education.

6.3 SOLID WASTE MANAGEMENT

Resource recovery, incineration and land disposal (landfilling and land spreading) are used in refineries for the management of solid wastes. The following is a brief review of these solid waste management methods and their applicability to coal conversion wastes.

6.3.1 Resource Recovery

From an environmental standpoint and when applicable, recovery of by-products from a waste or use of the waste as feedstocks in other processes would be the most desirable solid waste disposal option. In certain cases the value of the recovered material offsets the cost of the resource recovery operation. Processing of spent catalysts (especially those containing precious metals and chromium, nickel, and zinc) for catalyst rejuvenation or recovery of metals for reuse is commonly performed in a number of industries; catalyst reclamation is currently an established industry. Waste solvents can also be processed (e.g., by distillation) for solvent recovery or incinerated for heat recovery.

Catalysts used in refineries fall into three categories: noble metal catalysts containing platinum and palladium used in hydrogenation, alkylation and reforming; non-noble metal catalysts containing nickel, cobalt, molybdenum and tungsten used in hydrocracking, hydrotreating, and hydrorefining; and "inert" catalyst such as silica and alumina used in catalytic cracking and Claus plants. Because of the high price of noble metal catalysts, the first category of catalysts is almost invariably processed for metal recovery. The "inert" catalysts, which are relatively inexpensive, are commonly disposed of by landfilling. Some of the non-noble metal catalysts (catalysts in the second category) are currently processed for reuse and the interest in recycling other non-noble metal catalysts is growing due to increased catalyst usage, increasing metal values and stringent disposal regualtions(40).

The coal conversion catalysts which should be suitable for material recovery and recycling include shift and methanation catalysts in high Btu gasification and hydrotreating catalyst in coal liquefaction. The shift and hydrotreating catalysts are generally cobalt molybdate-based and the methanation catalysts are nickel-based materials. To date very few shift and methanation tests have been conducted on coal-derived gases. Because of the proprietary nature of catalyst formulations used in these tests, very few data are available on the metal content of spent catalysts and catalyst life and quantities which determine the suitability and economics of catalyst processing for material recovery. Spent methanation catalyst, although deactivated as far as catalytic activity for methanation is concerned, has considerable capacity for adsorption of sulfur compounds and can conceivably be used as a sulfur guard for the removal of trace sulfur in the methanator feed prior to ultimate disposal or processing for metal recovery. The suitability of spent catalyst for use as a methanation guard has not been evaluated.

Another specific example of resource recovery in petroleum refineries, which would have potential application in coal conversion, is the return of the oil recovered from wastewaters to the refinery for reprocessing. In coal conversion facilities which generate wastewaters containing appreciable quantities of oils and tars (e.g., coal gasification plants using the Lurgi technology and coal liquefaction plants), tars and oils recovered from the wastewaters can be returned to the process (e.g., injected into the gasifier or used for briquetting coal fines). The recovered tars and oils can also be incinerated on-site as fuel or sold for fuel use.

6.3.2 Incineration

Refinery wastes which have been reportedly disposed of by incineration include API separator bottoms, dissolved air flotation float, slop oil emulsion solids and waste biosludge(41). Major types of incinerators which are in commercial use for the disposal of municipal and industrial wastes are rotary kiln, multiple hearth furnace, fluidized bed and multiple chamber. Fluidized bed incineration is believed to be the most desirable incineration system for application to refinery wastes and has been reported to have been used in some refineries(24). Fluidized systems can provide adequate detention time, stable combustion temperatures, sufficient mixing and high heat transfer efficiency. Because of mixing and temperature uniformity in the fluidized bed, the volatilized hydrocarbons are ignited, thereby reducing or eliminating the possibility of creating an extremely dangerous explosive mixture of gaseous hydrocarbons and air. Experience with the incineration of refinery wastes indicates that a heating value of 4000 kcal/l (29,000 Btu/gal) is necessary for self-sustaining combustion(18). The normal range of operating temperatures is 977°K to 1088°K (1300°F to 1500°F).

Incineration can reduce the waste to an ash which, because of its small volume and inertness, can be more conveniently disposed of (e.g., in landfills). Incineration has proven to be very reliable and efficient and has been widely used for the disposal of a variety of industrial sludges and solids and municipal refuse and biosludges from the treatment of sanitary sewage. Nearly complete destruction of organics can be achieved in properly designed and operated incinerators. Compared to land disposal methods, incineration requires very little space. Except for potential air pollution problems, which can be controlled by use of good designs, afterburners and particulate control devices, and a possible fuel penalty when handling wastes with inadequate heat values, incineration is the most desirable disposal option (when resource recovery is inapplicable), especially for the destruction of hazardous organics.

Major coal conversion wastes which may be disposed of by incineration include tar and oil sludges, coal fines, chars and biosludges. The incineration of these wastes can be combined with on-site power generation or be carried out in a separate waste disposal incinerator. The type of incinerator most suitable for the disposal of these wastes, the optimum operating temperature and combustion residence time, and the required pollution control equipment must be established through bench-scale studies or test burns of the waste at existing commercial incinerators.

6.3.3 Land Disposal

Land disposal methods which have been used for refinery wastes include application of sludges to soils ("land spreading"), disposal of sludges and solid wastes in landfills and isolated burial of containerized and/or chemically fixed wastes.

When large land areas are available and the climate (rainfall, evaporation) and hydrogeological conditions (distance to groundwater; groundwater flow, type of soil and geological formation) are favorable, some organic and inorganic sludges may be disposed of by application to soil. The sludge is applied to the soil by "spreading" or "flooding," and is disked under and worked into the top soil. The organic component of the sludge undergoes biodegradation in the soil and eventually becomes part of the soil humus. Sludge disposal by application to soils has been used for the disposal of oily sludges from production and refining of crude oil and for the disposal of biosludges from refinery wastewater treatment(41,42). Coal conversion plant wastes which may be suitable for disposal by landspreading include bottom sludges from API separator, flotation and emulsion breaking units; oil stripper bottoms (e.g., in coal liquefaction and in some high Btu gasification processes); and biosludges. Although tar and oil sludges from petroleum refineries have been shown to be degradable when applied to soils, such sludges from coal gasification plants may be more resistant to degradation in the soil environment because of the highly aromatic nature of the organics in these sludges. The degradability of specific coal conversion wastes in the soil environment, the possible need for addition of supplementary nutrients and ammendments to soil and the appropriate rate and frequency of sludge application to soil would have to be determined using experimental plots representative of the disposal site. As with the application of wastewaters to soils (see Section 6.2.3), sites for land disposal of sludges can present an odor problem or result in the contamination of surface waters and groundwaters unless such sites are properly located, designed and operated.

Landfilling is the most widely used practice for the disposal of refinery process sludges and solid wastes. Landfills may be located on site (on or near the plant) or the waste may be hauled away in trucks to off-site municipal or industrial landfills.

In conventional landfilling (i.e., use of sanitary landfills) the waste is deposited in layers on land, compacted and covered with a layer of dirt. Sanitary landfills are widely used for the disposal of municipal and industrial refuse. Co-disposal of biological wastewater treatment sludges and municipal refuse is also practiced at a number of landfills. Provided that adequate measures are taken to reduce potential for the contamination of groundwaters and surface waters and to minimize nuisances associated with landfill operation, sanitary landfilling can be an environmentally acceptable and cost-effective method for solid waste disposal. To minimize the potential for the contamination of groundwaters and surface waters, landfills must be located in areas where the subsurface formation is relatively impervious to infiltration (e.g., dense clays) and where the distance to the groundwater table is significantly large. The landfill surface area should also be properly contoured to divert surface runoff from the site. When the subsurface formations do not provide adequate barriers against leachate infiltration, the use of artifical barriers such as plastic, asphalt, concrete or clay materials for lining the landfill may be necessary. The intercepted leachate would be pumped to a surface facility for treatment. Observation wells should also be installed downstream of the landfill site (in the direction of groundwater flow) to detect leachate migration.

Land burial is essentially one form of landfilling whereby the waste is deposited in a natural or man-made cavity in the ground and usually covered with dirt. In some applications ("pit disposal"), a wet sludge may be deposited in a pit and allowed to dry before the pit is covered with dirt and a new pit is excavated.

When highly hazardous wastes are to be disposed of in landfills, pretreatment of wastes involving chemical fixation and/or encapsulation may be used to minimize the potential for the release of waste components in the landfill environment via solubilization or chemical or biological processes. Both organic and inorganic materials have been used as chemical fixing agents. The fixing agents include: asphalt, epoxies, tars, Portland and other lime-based cements, and proprietary formulations (e.g., in the Chem-fix process). Raw or chemically fixed sludges can also be encapsulated in plastic, metal or concrete containers or coated with self-setting resins prior to disposal. Considerable effort is currently in progress on the amenability of various wastes to chemical fixation and on the effectiveness of various chemical fixation processes to reduce the leachability of the waste. The chemical fixation processes are generally expensive and their applications limited to small-volume high-toxicity wastes. An engineering estimate for the chemical fixation of flue gas desulfurization sludge, including final disposal, indicates a cost of $8 to $13/tonne ($9 to $14/ton)(43). In coal conversion, the most likely candidate waste stream for chemical fixation would be the spent catalysts which cannot be processed for material recovery.

When a coal conversion plant is located at some distance from the coal mine and suitable land is available, conventional landfilling would likely be employed for the disposal of bulk or chemically fixed solid wastes and sludges. When a plant is located within a reasonable transportation distance from the mine, return of the coal conversion solid wastes and sludges to the coal mine would be an attractive means for the disposal of such wastes, especially when area surface mining is practiced. Disposal in surface mines would essentially be one form of landfilling where the overburden material would be used as the cover material. The operation would be subject to the same restrictions cited above for sanitary landfills. When coal is deep mined, there would be a greater time delay before the waste can be deposited in the mine. In the case of deep mining, the physical operation of returning the waste to the mine would also be more difficult, requiring certain changes in mine design and operation to accommodate the space and equipment for returning the wastes. The return of ash and flue gas desulfurization sludges to the mines would have the potential benefit of reducing acid mine drainage formation. This would especially be the case in eastern mines where acid mine drainage is a major pollution problem.

7.0 HEALTH AND ECOLOGICAL EFFECTS OF SELECTED CONSTITUENTS IN REFINERY AND COAL CONVERSION PROCESS/WASTE STREAMS

7.1 PURPOSE AND SCOPE

Some of the components of refinery and coal conversion wastes have been shown to be highly hazardous due to their toxicity, carcinogenicity, mutagenicity and/or teratogenicity. Knowledge of the sources of these constituents, and their fate in the refinery and coal conversion processes and control operations, are necessary to assess the adequacy of the conventional control technologies for the removal of these constituents and the additional control technology requirements. As part of the present program for the assessment of the applicability of refinery control technologies to coal conversion, the major hazardous constituents common to both refinery and coal conversion were identified and their hazardous characteristics reviewed. The adequacy of the refinery control technologies judged to be applicable to coal conversion plants for the control of these constituents was assessed.

Table 7-1 lists the principal constituents of refinery streams which were identified in Section 4 as having counterparts in coal conversion plants. Many of these constituents (e.g., NO_x, H_2S, SO_2 and phenol) are not unique to refinery or coal conversion wastes and are emitted from a variety of industrial and nonindustrial (e.g., automobile) sources. Although some of these constituents are hazardous (some at very high concentration levels), they are not discussed in this section in any great detail because of their commonplace nature. The available data on health and environmental hazards associated with these ubiquitous chemicals, however, are summarized in Table 7-2, along with some pertinent occupational and environmental regulations.

Certain of the chemicals listed in Table 7-1 are relatively unique to refinery and coal conversion wastes and are highly hazardous. These chemicals fall into three classes, namely polynuclear aromatic hydrocarbons (PAH), heavy metals and organometallic compounds, and low molecular weight aromatic

TABLE 7-1. PRINCIPAL CONSTITUENTS OF REFINERY STREAMS HAVING COUNTERPARTS IN COAL CONVERSION WASTE STREAMS

Stream	Constituents
Gaseous	
Sulfur-containing species	H_2S, SO_2, SO_3, CS_2, COS, S_8 (vapor/mist)
Nitrogen-containing species	NH_3, NO_x
Carbon oxides	CO, CO_2
Organics	Alkanes (methane through hexane) Aldehydes (e.g., HCHO) Acids (e.g., propionic acid) Low molecular weight aromatics (e.g., benzene, toluene and xylene) Particulate matter, including PAH; organometallics
Miscellaneous	H_2, N_2, H_2O
Liquid	
Dissolved gases	NH_3, H_2S, HCN
Inorganic anions	Cl^-, $SO_4^=$, $PO_4^=$, NO_2^-, NO_3^-
Inorganic cations	Ca^{++}, Mg^{++}, Cu^{++}, Fe^{++}, Fe^{+++}, Zn^{++}
Organic compounds	Phenolics, mercaptans, oil, low molecular weight aromatics (e.g., benzene, toluene, xylene)
Other parameters	TSS, TDS, alkalinity, radioactivity
Solid	
Organics	Phenols, benzo-a-pyrene, other PAH and aromatic compounds
Heavy metals	Ni, V, Co, Mo, As, Se, Hg, Be, Cr, Cu, Zn, Ag, Cd, Pb
Miscellaneous species/ parameters	SiO_2, acids, alkali, miscellaneous process and treatment chemicals, biomass, inerts, radioactivity

TABLE 7-2. SUMMARY OF HAZARDOUS PROPERTIES OF SOME UBIQUITOUS CONSTITUENTS OF REFINERY AND COAL CONVERSION WASTES(44,45)

Property	Constituent		
	H_2S	SO_2	SO_3
MEG Category*	53	53	53
MEG Hazard Indicator†	NH	--	--
Toxic Dosage‡	Inhalation,human-LCLo,600 ppm/30 min. Inhalation,rat-LC50,713 ppm/1 hr. Inhalation,mouse-LC50,673 ppm/1 hr.	Inhalation,human-TCLo,3 ppm/5 day Inhalation,rat-LCLo,611 ppm/5 hr. Inhalation,mouse-LCLo,763 ppm/20 min. Inhalation,guinea pig-LCLo,5000 ppm/5 min.	Aquatic toxicity,TLm 96: 100-10 ppm
Toxicology	• An irritant and asphyxiant. • High concentrations result in dizziness, diarrhea, and dysuria. Paralysis of the respiratory system may be fatal.	• Concentrations of 6-12 ppm cause irritation of nose and throat. • Concentrations of 20 ppm and greater are irritating to the eye. • Affects upper respiratory tract and bronchial tubes. • 400-500 ppm may be fatal.	--
Toxic Hazard Rating§			
Acute Local	Irritant - 3	Irritant - 3; Inhalation - 3; Ingestion - 3	Irritant - 3; Inhalation - 3; Ingestion - 3
Acute Systemic	Inhalation - 3	U	U
Chronic Local	U	Irritant - 2; Inhalation - 2	Irritant - 2; Inhalation - 2
Chronic Systemic	Inhalation - 3	U	U
Fire Hazard**	Dangerous	--	--
Explosion Hazard**	Moderate	--	--
Disaster Hazard**	Highly dangerous (may emit SO_x fumes; can react vigorously with oxidizing materials)	Dangerous; reacts with water/steam to product toxic fumes	Dangerous; reacts with steam to produce H_2SO_4
Standards and Regulations			
OSHA			
Air, ceiling conc.	20 ppm	--	--
Air, peak conc.	50 ppm/10 min.	--	--
Air, TLV	10 ppm (~15 mg/m^3)	--	--
Air, TWA††	--	5 ppm	--
NIOSH Criteria Documents			
Air, TWA††	--	2 ppm	--
Air, ceiling conc.	--	--	--

(continued)

TABLE 7-2. CONTINUED

Property	Constituent		
	CS_2	COS	CO
MEG Category*	53	53	42
MEG Hazard Indicator†	NH	NH	NH
Toxic Dosage‡	Oral,human-LDLo, 14 mg/kg Intraperitoreal,rat-LDLo,400 mg/kg Subcutaneous,rabbit-LDLo,300 mg/kg Aquatic toxicity,TLm96:1000-100 ppm Inhalation,human-LCLo,4000 ppm/30 min. Inhalation,human-TCLo,50 mg/m^3/7 yr.	Inhalation,mouse-LCLo,2900 ppm	Inhalation,dog-LCLo,3841 ppm/46 min. Inhalation,cat-LCLo,8730 ppm/35 hr. Inhalation,guinea pig-LC50,2444 ppm/4 hr Inhalation,human-LCLo,4000 ppm/30 min. Inhalation,rat-LC50,1807 ppm/4 hr. Inhalation,mouse-LC50,5718 ppm/4 hr. Inhalation,human-TCLo,650 ppm/45 min.
Toxicology	• Acute poisoning may result in depression, stupor, followed by unconsciousness and possibly death. • Chronic poisoning causes disturbances of central nervous system.	• Narcotic in high concentrations.	• Combines with hemoglobin, resulting in asphyxia. • Concentrations of 4,000 ppm fatal in less than an hour. • Chronic exposure results in auditory disturbances, glycosuria, and heart irregularities.
Toxic Hazard Rating§			
Acute Local	Irritant - 1	Irritant - 1; Ingestion - 1; Inhalation - 1	0
Acute Systemic	Ingestion - 3; Inhalation - 3; Skin Absorption - 3	Inhalation - 3	Inhalation - 3
Chronic Local	U	Irritant - 1; Inhalation - 1	0
Chronic Systemic	Ingestion - 3; Inhalation - 3; Skin Absorption - 3	Inhalation - 3	Inhalation - 1
Fire Hazard**	Highly dangerous	Dangerous	Dangerous
Explosion Hazard**	Severe	Moderate	Severe
Disaster Hazard**	Highly dangerous; emits SO_x fumes; can react vigorously with oxidizing materials	Dangerous; reacts with oxidizing materials; may emit H_2S.	--
Standards and Regulations			
OSHA			
Air, ceiling conc.	30 ppm	--	--
Air, peak conc.	100 ppm/30 min.	--	--
Air, TLV	--	--	--
Air, TWA††	20 ppm	--	50 ppm
NIOSH Criteria Documents			
Air, TWA††	--	--	35 ppm
Air, ceiling conc.	--	--	200 ppm

(continued)

TABLE 7-2. CONTINUED

Property	Constituent		
	CO_2	NH_3	NO
MEG Category*	42	47	47
MEG Hazard Indicator†	NH	NH	--
Toxic Dosage‡	Inhalation,rabbit-TCLo,10 pph/7-12 days Inhalation,rat-LCLo,657,190 ppm/15 min	Inhalation,rabbit-TCLo,10,066 ppm/hr Inhalation,human-LCLo,10,000 ppm/3 hr. Inhalation,mouse-LC50,4837 ppm/1 hr Inhalation,human-TCLo, 20 ppm Aquatic toxicity,TLm96:10-1 ppm	Inhalation,mouse-LCLo,320 ppm Inhalation,rabbit-LC50,315 ppm/15 min.
Toxicology	• Considered a simple asphyxiant; symptoms include headache, dizziness, muscular weakness, and drowsiness. • Contact of CO_2 "snow" may cause skin "burns."	• Irritating to the eyes and mucous membranes of respiratory tract. • Symptoms include irritation of the eyes, conjunctivitis, irritation of the nose and throat, coughing and vomiting.	--
Toxic Hazard Rating§			
Acute Local	0	Irritant - 3; Ingestion - 3; Inhalation - 1	Irritant - 3
Acute Systemic	Inhalation - 1	U	Ingestion - 3; Inhalation - 3
Chronic Local	0	Irritant - 1	U
Chronic Systemic	Inhalation - 1	U	Ingestion - 2; Inhalation - 2
Fire Hazard**	--	Moderate	--
Explosion Hazard**	--	Moderate	--
Disaster Hazard**	Slight	Moderate; emits toxic fumes	Dangerous; reacts with reducing materials
Standards and Regulations			
OSHA			
Air, ceiling conc.	--	--	--
Air, peak conc.	--	--	--
Air, TLV	--	--	--
Air, TWA††	5000 ppm	50 ppm	25 ppm
NIOSH			
Air, TWA††	--	--	25 ppm
Air, ceiling conc.	--	50 ppm	--

(continued)

TABLE 7-2. CONTINUED

Property	Constituent		
	NO_2	HCHO	$CH_3CH_2CO_2H$
MEG Category*	47	7A	8A
MEG Hazard Indicator†	--	X	--
Toxic Dosage‡	Inhalation, human-TCLo, 64 ppm Inhalation,rat-LC50,80 ppm/4 hr. Inhalation,mouse-LCLo,220 ppm/30 min. Inhalation,monkey-LCLo,44 ppm/6 hr. Inhalation,rabbit-LC50,315 ppm/15 min.	Inhalation,human-TCLo,13.8 ppm Inhalation,rat-LCLo,250 ppm/4 hr. Inhalation,mouse-LCLo,900 mg/m^3/2 hr. Aquatic toxicity, TLm96:100-10 ppm Inhalation,cat-LCLo,820 mg/m^3/8 hr. Oral,rat-LD50,800 mg/kg	Aquatic toxicity, TLm96:1000-100 ppm Oral,rabbit-LD50,1510 mg/kg
Toxicology	--	• Toxic effects are mainly those of irritation. • Ingestion causes violent vomiting and diarrhea. • A suspected carcinogen of the lung.	• Low toxicity based on animal experiments.
Toxic Hazard Rating§			
Acute Local	Irritant - 3	Irritant - 3; Allergen - 1	Irritant - 2
Acute Systemic	Ingestion - 3; Inhalation - 3	Ingestion - 3; Inhalation - 3	Ingestion - 1
Chronic Local	U	Allergen - 1	Irritant - 1
Chronic Systemic	Ingestion - 2; Inhalation - 2	U	Ingestion - 1
Fire Hazard**	--	Moderate	Moderate
Explosion Hazard**	--	Dangerous when heated above flash point	--
Disaster Hazard**	Dangerous; reactive with reducing materials	Moderately dangerous	Slight; emits acrid fumes
Standards and Regulations			
OSHA			
Air, ceiling conc.	--	5 ppm	--
Air, peak conc.	--	10 ppm/30 min/8 hr	--
Air, TLV	--	--	--
Air, TWA††	5 ppm	3 ppm	--
NIOSH Criteria Documents			
Air, TWA††	--	--	--
Air, ceiling conc.	1 ppm	--	--

(continued)

TABLE 7-2. CONTINUED

Property	Constituent		
	SiO_2	Phenol	CH_3SH
MEG Category[*]	43	18A	13A
MEG Hazard Indicator[†]	--	NH	NH
Toxic Dosage[‡]	Intraperitoneal-rat, LCLo-400 mg/kg	Oral,human-LDLo,14 mg/kg Oral,human-LDLo,140 mg/kg Oral,rat-LD50,414 mg/kg Subcutaneous,rat-LDLo,650 mg/kg Aquatic toxicity-TLm96:100-10 ppm	Inhalation,rat-LCLo,10,000 ppm Subcutaneous,mouse-LD50,2.4 mg/kg
Toxicology	• Chief cause of industrial pulmonary dust disease. • Results in silicosis and modular fibrosis in the lungs.	• In acute poisoning, major effect is on central nervous system; damage to kidney, liver, pancreas, spleen and edema of lungs may result. May be fatal. • Chronic poisoning may result in diarrhea, digestive disturbance, nervousdisorders and skin eruptions.	--
Toxic Hazard Rating[§]			
Acute Local	Inhalation - 2	Irritant - 3; Ingestion - 3; Inhalation - 3	Irritant - 2
Acute Systemic	0	Ingestion - 3; Inhalation - 3; Skin Absorption - 3	Ingestion - 2; Inhalation - 2
Chronic Local	Inhalation - 3	Irritant - 2	U
Chronic Systemic	Inhalation - 1	Ingestion - 2; Inhalation - 2; Skin Absorption - 2	U
Fire Hazard[**]	--	--	Unknown
Explosion Hazard[**]	Moderate	Dangerous; may react with oxidizing materials.	Dangerous; on decomposition, emits SO_x fumes; will react with water, steam or acids to produce toxic and flammable vapors; can react vigorously with oxidizing materials.

(continued)

TABLE 7-2. CONTINUED

Property	Constituent		
	SiO_2	Phenol	CH_3SH
Standards and Regulations			
OSHA			
Air, ceiling conc.	--	--	10 ppm
Air, peak conc.	--	--	--
Air, TLV	--	--	--
Air, TWA††	80 mg/m^3/%SiO_2	5 ppm (skin)	--
Niosh Criteria Documents			
Air, TWA††	--	--	--
Air, ceiling conc.	--	--	--

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*Multimedia Environmental Goals (MEGs) are levels of significant contaminants or degradents (in ambient air, water, or land or in emissions or effluents conveyed to the ambient media) that are judged to be (a) appropriate for preventing certain negative effects in the surrounding populations or ecosystems, or (b) representative of the control limits achievable through technology. EPA has published MEG values for more than 650 pollutants(50).

†A rating system has been developed by EPA for assigning indicators (X = hazardous, XX = very hazardous; XXX = most hazardous; or NH - nonhazardous) to designate potentially hazardous substances based on values generated by the MEGs methodology(50). A dash (--) indicates substances for which hazard rankings have not yet been developed. A revised and expanded system of categorization and hazard ranking is currently being developed for EPA by Research Triangle Institute (57); the revised MEG system for organic compounds is expected to be completed within 1-2 months, while the revised system for inorganic compounds will be completed at a later date.

‡LCLo - lowest published lethal concentration; LC50 - lethal concentration, 50 percent kill; LD50 - lethal dose, 50 percent kill; LDLo - lowest published lethal dose; TCLo - lowest published toxic concentration; TDLo - lowest published toxic dose.

§Toxic hazard rating code:
0 - None: (a) no harm under any conditions; (b) harmful only under unusual conditions or overwhelming dosage.
1 - Slight: causes readily reversible changes which disappear after end of exposure.
2 - Moderate: May involve both irreversible and reversible changes not severe enough to cause death or permanent injury.
3 - High: May cause death or permanent injury after very short exposure to small quantities.
U - Unknown: No information on humans considered valid by authors (Reference 45).

**Hazard applies to conditions of exposure to heat or flame.

††TWA - time weighted average.

compounds, and are discussed in the following sections. The discussion addresses the sources, characteristics and health effects of these chemical classes, and control technology requirements.

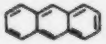
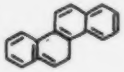
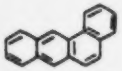
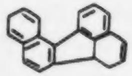
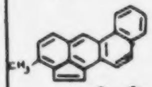
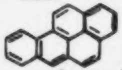
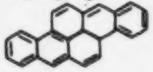
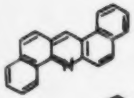
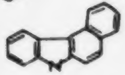
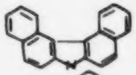
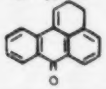
7.2 POLYCYCLIC AROMATIC HYDROCARBONS (PAH)

As indicated in Table 7-1, PAH emissions are generally associated with gaseous and solid waste streams in petroleum refineries. In petroleum refining the primary source of PAH emissions is the regeneration of the cracking catalysts. Regeneration consists of combusting the carbonaceous material that accumulates on the catalyst surface. PAHs are discharged both from the regenerator unit and from the regenerator unit incinerator waste heat boilers. The majority of PAH compounds generated are adsorbed on particulate matter. PAH compounds have also been detected in high boiling petroleum-derived oils (b.p. 370°C) obtained from crude oil by catalytic cracking. Petroleum crude is also estimated to contain approximately 1 ppm of the PAH compound benzo(a)-pyrene(46,47).

Since the organic portion of coal is largely composed of polynuclear aromatic structures, it is not surprising that polynuclear aromatic hydrocarbons are present in coal conversion wastes. In addition to particulate matter, PAHs are associated with the heavier and more aromatic fractions of coal conversion streams (e.g., tars, oils, etc.). The formation of PAHs in coal conversion processes has been documented(48) and several studies have been undertaken for their identification and characterization in a number of waste streams at pilot gasification plants. PAHs have been detected in atmospheric particulate matter at coal liquefaction plants(48). Mass spectroscopic analyses of tars produced in a Synthane gasifier have indicated the presence of PAHs(49). In general, the quantities, chemical structures and fate of PAHs in coal conversion operations are not well-defined and are expected to vary among different plants depending on the type of coal used, coal conversion process employed and operating conditions.

PAH compounds are of particular environmental concern because of their carcinogenicity. Table 7-3 presents seven classes of PAH compounds which are known or suspected carcinogens and which are associated with coal conversion processes and/or refineries and some toxicity data for these compounds. The

TABLE 7-3. CLASSES OF KNOWN OR SUSPECTED CARCINOGENIC PAH AND ANALOG COMPOUNDS ASSOCIATED WITH PROCESSING AND UTILIZATION OF PETROLEUM AND/OR COAL AND TOXICITY DATA*(49,44)

Compound Class	Representative Compound	Structure	Toxic Dosage*	MEG Category	MEG Hazard Indicator
Polynuclear Aromatic Hydrocarbons, PAH					
Anthracenes	anthracene		Oral,rat-TDLo,18 g/kg/78 wks; subcutaneous,rat-TDLo,3300 mg/kg/33 wks	21	NH
Chrysenes	chrysene		Subcutaneous,mouse-TDLo,300 mg/kg; skin,mouse-TDLo,99 mg/kg/31 wks	21	NH
Benzanthracenes	benzo(a)anthracene		Skin,mouse-TDLo, 2 mg/kg; intraveneous,mouse-LDLo,10 mg/kg; parenteral,mouse-TDLo,8 mg/kg; implant,mouse-TDLo,80 mg/kg	21	XX
Fluoranthenes	benzo(j)fluoranthene		Skin,mouse-TDLo,228 mg/kg/24 wks	22	NH
Cholanthrenes	20-methylchlolanthrene		Oral,rat-TDLo,280 mg/kg; oral,mouse-TDLo,40 mg/kg; skin,mouse-TDLo,13 mg/kg/42 wks	22	NH
Benzopyrenes	benzo(a)pyrene		Oral,rat-TDLo,4563 mg/kg/53 wks; skin,rat-TDLo,44 mg/kg/22 wks; intraveneous,rat-TDLo,39 mg/kg/6 days	21	XXX
Dibenzpyrenes	dibenzo(a,h)pyrene		Skin,mouse-TDLo,165 mg/kg/24 wks	21	NH
Heterocyclic and Oxidized Analogs of PAHs (N, S, and O-Containing Compounds)					
Mono-and dibenzacridines	dibenz(a,h)acridine		Oral,mouse-TDLo,18 g/kg/89 wks; skin,mouse-TDLo,700 mg/kg/29 wks; subcutaneous,mouse-TDLo,450 mg/kg/24 wks; intraveneous,mouse-TDLo,10 mg/kg	23B	X
Benzocarbazoles	7H-benzo(c)carbazole		Subcutaneous,mouse-TDLo,120 mg/kg/12 wks	23C	-
Dibenzocarbazoles	7H-dibenz(c,g)carbazole		Subcutaneous,rat-TDLo,150 mg/kg/17 wks; oral,mouse-TDLo,400 mg/kg/23 wks; intraveneous,mouse-TDLo,10 mg/kg	23C	X
Benzathrones	7H-benz(d,e)anthracen-7-one		Intraperitoneal,mouse-LDLo,1000 mg/kg	24	NH

*See footnotes to Table 7-2 for definition and explanation of terms.

data in the table include the EPA Multimedia Environmental Goals (MEG) and MEG Hazard Indicators for each class of compounds (see footnotes to Table 7-2). One of the best characterized PAH compounds is benzo(a)pyrene, which has been determined to be extremely carcinogenic to experimental animals, can induce a cancerous skin tumor in mice when only 0.25 mg is injected subcutaneously and has recently been established as a human carcinogen. Benzo(a)pyrene is the most widely accepted indicator of PAH content and biological activity. In addition to PAHs there are numerous heterocyclic and oxidized analogs of PAH compounds, some of which may be found in petroleum and coal conversion wastes (see Table 7-3).

Most of the available epidemiological and laboratory studies relating to the carcinogenic properties of PAH have been in connection with the coking industry and other coal carbonization/hydrogenation processes. Comparatively little epidemiological work has been reported on petroleum refinery workers. A number of epidemiological studies and laboratory testing (mostly in connection with coal hydrogenation and Fischer-Tropsch synthesis) are reviewed in Reference 49.

Several recent investigations of the toxicological and biological significance of PAH have centered on synfuel-related materials. Two such studies are conducted at Oak Ridge National Laboratory, Oak Ridge, Tennessee(47) and at the National Cancer Institute, Bethesda, Md.(51). At Oak Ridge the carcinogenic activity has been observed for three-, four- and five-ring PAHs from synfuels materials. The specific activity has been found to be the greatest for the four-ring and five-ring PAH fractions containing the most common known carcinogens (e.g., benzo(a)pyrene, benzo(c)phenanthrene, 3-methylcholanthrene, etc.). At the National Cancer Institute, the carcinogenicity activation mechanism, metabolism, macromolecular binding, cellular effects, and mutagenicity of PAHs are under study. These studies include in vitro testing and analytical methods development. As indicated above, PAH compounds in gaseous streams are generally associated with particulate matter. Particulates by themselves can also be hazardous to human health by virtue of their fine size which allows them to penetrate deep into the lungs.

NIOSH has recently developed criteria and recommended a standard for occupational exposure to coal tar products, including PAH(52). The recommended standard is 0.1 mg/m^3 of a cyclohexane extract fraction of a coal tar sample, determined as the time-weighted average concentration for up to a 10-hour work shift in a 40-hour work week. Several Federal, state and local air quality standards have also been promulgated for control of particulate emissions per se. These include New Source Performance Standards for particulate matter for petroleum refineries, which restrict particulate emissions to 1.0 kg/1000 kg of coke burn-off in catalyst regeneration.

7.3 HEAVY METALS AND ORGANOMETALLIC COMPOUNDS

As indicated in Table 7-1, heavy metals and organometallic compounds are found in liquid, solid and gaseous waste streams generated at petroleum refineries. The refinery solid wastes having the highest concentrations of heavy metals are the spent catalysts, coker fines and crude oil storage sediments. Noble and non-noble heavy metals are utilized as catalysts in refinery operations. Noble metal catalysts such as platinum and palladium are recycled and/or recovered because of their economic value. Non-noble metals (e.g., cobalt, molybdenum, chromium, tungsten, nickel and vanadium) are sometimes reprocessed, depending upon catalyst price, or may be discharged as solid wastes. Coker fines and crude oil storage sediments contain arsenic and heavy metals listed in Table 7-1. Heavy metals may also be discharged as volatile or particulate emissions in refinery operations (e.g., during catalyst regeneration and fuel combustion). The quantities and composition of heavy metals discharged in the various gaseous, solid and liquid waste streams in refinery operations are primarily functions of both the composition of the crude oil processed and the catalysts employed.

The chemical nature of coal combined with the conditions under which it is gasified or liquefied are conducive to the release of numerous heavy metals and their compounds. (Elemental analyses of a variety of coals have revealed the presence of over one-half the elements of the periodic table, many of them heavy metals.) As with refinery waste streams, heavy metals are present in liquid, gaseous and solid streams from coal conversion operations. Solid wastes containing heavy metals will include coal/char fines and ash produced in gasification, and spent catalysts and sludges from gas purification and upgrading operations. Spent catalysts from shift conversion operations are primarily cobalt molybdate based materials that are contaminated with coal derived trace elements and occluded high molecular weight organics. Spent methanation catalysts are primarily nickel-based materials, and also may be contaminated with organics and trace-elements from coal. Coal/char fines, ash and process sludges will contain coal-derived metals, especially less volatile elements (Ni, Be, and Cr). As with refinery operations, heavy metals may also be discharged as volatiles or particulates.

Heavy metals are of particular environmental concern because of their toxicological properties and their known or suspected carcinogenicity. Table 7-4 presents major metallic elements associated with refineries and coal conversion processes, and some toxicity data for these elements.* Several of these metals are known or suspected carcinogens as indicated in Table 7-4. In general, the toxicities and properties of heavy metals and heavy metal compounds vary widely and cannot be generalized.

Petroleum refining and coal gasification and liquefaction are conducive to the formation of a variety of organometallic compounds. Little work has been performed to date to elucidate the nature and toxicological effects of organometallics that may be produced in these processes. Some of the major types of organometallic compounds that may be formed are: metal carbonyls; metallocenes; arene carbonyls; metal alkyls; metal porphyrins; metal hydrides; and metal chelates. To date, only metal porphyrins and metal carbonyls have been detected in petroleum refinery streams. However, the presence of the remaining organometallics cannot be completely discounted. Descriptions of these organometallic compounds can be found in the literature(53).

Table 7-5 presents toxicity data on specific organometallic compounds which are representative of several of the seven classes mentioned above, and which have been detected or are likely to be present in petroleum refinery and coal conversion wastes.

7.4 AROMATIC COMPOUNDS

The third category of chemical compounds which poses environmental hazards in both refinery and coal conversion operations is low molecular weight aromatic compounds. As indicated in Table 7-1, low molecular weight aromatics (e.g., benzene, toluene, xylene and related compounds) are associated primarily

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*Although in chemical terminology arsenic is not considered a metal, it is grouped with metallic elements here for discussion purposes.

TABLE 7-4. SUMMARY OF TOXICOLOGICAL AND ENVIRONMENTAL DATA FOR MAJOR HEAVY METALS ASSOCIATED WITH REFINERY AND COAL CONVERSION OPERATIONS(44,45)

	Metal		
Parameter*	As	Co	Ni
MEG Category	49	74	76
MEG Hazard Rating	XXX	XX	XXX
Toxic Dosage	Intramuscular,rat-LDLo,25 mg/kg Subcutaneous,rabbit-LDLo,300 mg/kg Intraperitoneal,guinea pig-LDLo,10 mg/kg Subcutaneous,guinea pig-LDLo,300 mg/kg	Oral,LDLo-1500 mg/kg Intramuscular,rat-TDLo,112 mg/kg Intraperitoneal,mouse-LD50,22 mg/kg Oral,rabbit-LDLo,20 mg/kg	Inhalation,rat-TCLo,15 mg/m^3 Subcutaneous,rat-TDLo,15 mg/kg/6 wks Intramuscular,rat -LDLo,25 mg/kg Intratracheal,rat-LDLo,12 mg/kg Oral,guinea pig-LDLo, 5 mg/kg Inhalation,guinea pig-TCLo,15 mg/m^3/9 wks Intramuscular,hamster-TDLo,208 mg/kg/22 wks
Toxicology	• Considered highly toxic • Acute As poisoning results in stomach irritation and intestinal problems with nausea, vomiting and diarrhea. • Chronic As poisoning produces loss of appetite, cramps, nausea, constipation or diarrhea. Liver damage may occur, resulting in jaundice. • A recognized carcinogen of skin, lungs and liver.	• Considered to have low human toxicity when administered orally. • May result in hematologic, digestive and pulmonary changes in humans.	• Ingestion of large doses causes intestinal disorders, convulsions and asphyxia • A recognized carcinogen of the nasal cavity, paranasal sinuses and lungs. • Chronic exposure may result in a form of dermatitis.
Carcinogenic	yes (suspected)	yes (suspected)	yes (suspected)
Toxic Hazard Rating			
Acute Local	Irritant - 2; Allergen - 2; Ingestion - 3	Allergen - 1	Irritant - 1; Allergen - 1
Acute Systemic	Ingestion - 3; Inhalation - 3	Ingestion - 1; Inhalation - 1	Ingestion - 1; Inhalation - 3
Chronic Local	Irritant - 2; Allergen - 3	U	Irritant - 3; Allergen - 1
Chronic Systemic	Ingestion - 3; Inhalation - 3	U	Inhalation - 3; Ingestion - 3
Fire Hazard	Moderate when in the form of dust	Moderate	--
Explosion Hazard	Slight, in the form of dust	--	--
Disaster Hazard	Dangerous, can react vigorously on contact with oxidizing materials	--	--
Standards and Regulations			
OSHA			
Air, TWA	500 mg/m^3	100 mg/m^3	1 mg/m^3 (skin)
Criteria Document			
Air, ceiling conc.	2 mg/m^3	--	--

(continued)

TABLE 7-4. CONTINUED

	Metal		
Parameter*	Cr	Pb	Zn
MEG Category	68	46	81
MEG Hazard Indicator	XXX	XX	NH
Toxic Dosage	Inhalation,human-TDLo,4500 mg/m^3/5yr Intraveneous,rat-TDLo,2 mg/kg/6 wks Implant,rat-TDLo,1 mg/kg/6wks Intraperitoneal,mouse-LD50,102 mg/kg	Not available	Intraperitoneal,mouse-LD50,15 mg/kg
Toxicology	• Essentially non-toxic in the metallic form. • Chromic acid and salts have corrosive action on the skin and mucous membranes. Chromate salts are recognized carcinogens of the lungs, nasal cavity and paranasal sinuses.	• Lead poisoning is one of the commonest of occupational diseases. • Is a cumulative poison • Common clinical types of lead poisoning may be classified as: (a) alimentary; (b) neuro-motor; and (c) encephalic.	• Not inherently toxic; when heated, may evolve a fume of zinc oxide dust. • In small doses, zinc salts may produce digestive disorders. • Workers with zinc have been reported as suffering from a variety of non-specific intestinal, respiratory and nervous systems.
Carcinogenic	yes (suspected)	yes (suspected)	yes (suspected)
Toxic Hazard Rating			
Acute Local	Irritant - 3; Ingestion - 3; Inhalation - 3	0	--
Acute Systemic	U	Inhalation - 3; Inhalation - 3	--
Chronic Local	Irritant - 3; Ingestion - 3; Inhalation - 3	0	--
Chronic Systemic	Ingestion - 3; Inhalation - 3	Ingestion - 3; Inhalation - 3; Skin Absorption - 3	--
Fire Hazard	Moderate, in the form of dust.	Moderate	Moderate
Explosion Hazard	--	Moderate	Slight, when in the form of dust.
Disaster Hazard	--	Dangerous; can react vigorously with oxidizing materials.	--
Standards and Regulations			
OSHA			
Air, TWA	1 mg/m^3	200 mg/m^3	--
Criteria Document			
Air, TWA	--	150 mg/(Pb)m^3	--

(continued)

TABLE 7-4. CONTINUED

Parameter*	Metals	
	Mo	V
MEG Category	69	65
MEG Hazard Indicator	NH	X
Toxic Dosage	Intraperitoneal,mouse-LD50,160 mg/kg Subcutaneous,mouse-LD50,266 mg/kg	Not available
Toxicology	• No known cases of industrial poisoning by Mo have been reported. • Not stored by the body, but is rapidly excreted.	• V compounds act chiefly as irritants to conjunctival and respiratory tract. • Prolonged exposures may lead to pulmonary disorders, anemia, pallor and emaciation, and gastrointestinal disorders.
Carcinogenic	No	No
Toxic Hazard Rating		
Acute Local	Irritant - 1	--
Acute Systemic	U	--
Chronic Local	U	--
Chronic Systemic	Inhalation - 1	--
Fire Hazard	Moderate, in the form of dust.	Moderate, in the form of dust.
Explosion Hazard	Slight, in the form of dust.	--
Disaster Hazard	--	--
Standards and Regulations		
OSHA		
Air, TWA	--	--
Criteria Document		
Air, ceiling conc.	--	--

*For definition of terms and explanation of ratings, see Table 7-2.

TABLE 7-5. TOXICOLOGICAL DATA ON SELECT ORGANOMETALLICS ASSOCIATED WITH REFINERY AND/OR COAL CONVERSION WASTE STREAMS(44,45)

Parameter*	Compound		
	$Ni(CO)_4$	$Fe(CO)_5$	$Co_4(CO)_{12}$
MEG Category	76	72	74
MEG Hazard Indicator	XX	--	--
Toxic Dosage	Inhalation,rat -LC50,240 mg/m^3/30 min. Subcutaneous,rat-LD50,63 mg/kg Intraveneous,rat-LD50,66 mg/kg Inhalation,mouse-LC50,67 mg/m^3/30 min. Inhalation,dog-LCLo,360 ppm/90 min. Inhalation,cat-LC50,1900 mg/m^3/30 min. Aquatic toxicity,TLm96,100-10 ppm	Inhalation,rat-LCLo,33 ppm/330 min. Inhalation,mouse-LC50,7 mg/m^3 Oral,rabbit-LDLO,18 mg/kg Skin,rabbit-LD50,240 mg/kg Intraveneous,rabbit-LDLo,17 mg/kg Oral,guinea pig-LDLo,36 mg/kg Oral,rabbit-LD50,0.01 mg/kg	Inhalation,rat-LC50,1400 mg/m^3
Toxicology	• Toxic symptoms from inhalation are believed to be caused by both nickel and CO when liberated in the lungs. • In severe acute cases there is headache, dizziness, nausea, vomiting, fever, and difficult breathing. • Chronic exposure leads to cancer of respiratory tract and nasal sinuses.	• Inhalation causes dizziness, nausea, vomiting, followed by unconsciousness. • In fatal cases, death occurs from the 4th to 11th day with pneumonitis and injury to kidneys, liver and brain. • Less toxic than nickel carbonyl.	• Highly toxic.
Carcinogenicity	Yes	No	No
Toxic Hazard Rating			
Acute Local	Inhalation - 3	Irritant - 1	U
Acute Systemic	Inhalation - 3	Ingestion - 3; Inhalation - 3; Skin Absorption - 3	U
Chronic Local	U	U	U
Chronic Systemic	U	U	U
Fire Hazard	Dangerous	Dangerous	Dangerous
Explosion Hazard	Moderate	Moderate	Moderate
Disaster Hazard	Dangerous	Dangerous; can react vigorously with oxidizing materials	Dangerous
Standards and Regulations			
OSHA			
Air, TWA	7 mg/m^3	--	Not known
Air, TLV	--	10 ppb	--

(continued)

TABLE 7-5. CONTINUED

Parameter*	Compound	
	Ferrocene	Tetraethyl Lead
MEG Category	26B	26A
MEG Hazard Indicator	NH	X
Toxic Dosage	Oral,rat -LD50,1320 mg/kg Intraperitoneal,rat-LD50,50 mg/kg Oral,mouse-LD50,1550 mg/kg Intraperitoneal,mouse-LD50,335 mg/kg	Oral,rat-LDLo,17 mg/kg Inhalation,rat-LC50,6 ppm Intraperitoneal,rat-LDLo,10 mg/kg Subcutaneous,mouse-LDLo,86 mg/kg Skin,dog-LDLo,500 mg/kg Intraveneous,rabbit-LDLo,23 mg/kg Aquatic-TLm96, under 1 ppm
Toxicology	• Toxicity considered low.	• A powerful poison and solvent for fatty material. • Decomposes to form elemental lead, which may accumulate in body tissues. • Absorbed rapidly through the skin and lungs, and may be selectively absorbed by the central nervous system. • Produces brittleness of red blood cells. • Severe doses lead to several types of poisoning; (a) alimentary; (b) neuromotor; and (c) encephalic.
Carcinogenicity	No	Yes
Toxic Hazard Rating		
Acute Local	U	U
Acute Systemic	U	U
Chronic Local	U	U
Chronic Systemic	U	U
Fire Hazard	Moderate	Moderate
Explosion Hazard	--	--
Disaster Hazard	Dangerous; emits toxic fumes when heated.	Dangerous; can react vigorously with oxidizing materials.
Standards and Regulations		
OSHA		
Air, TWA	Not Known	--
Air, TLV	--	--

*For definition of terms and ratings, see Table 7-2.

with the liquid and gaseous streams (e.g., sour waters and oily waters) in both technologies. As discussed in Section 4.2.3, the liquid wastes containing low molecular weight aromatics generated in coal conversion processes will differ in aromatic content from those in refineries. Oily waters and tars generated in coal conversion operations will contain significantly higher concentrations of complex tars and aromatic compounds than refinery oily waters which contain primarily paraffinic and olefinic compounds.

Table 7-6 presents some of the available toxicological and environmental data for the principal aromatic compounds of concern. Of the compounds listed in the table, benzene and the aromatic amines (aminobenzenes, naphthylamines) are known or suspected carcinogens. Aromatic amines, particularly low molecular weight amines, are primarily associated with coal conversion processes although aniline and other low molecular aromatic amines have been detected in petroleum refinery wastes(49). The majority of amines generated in refinery operations are aliphatic rather than aromatic amines (e.g., diethylamine, triethylamine, tri-n-butylamine, etc.).

Environmental, epidemological, and biological data and Federal regulations and standards for low molecular weight aromatic compounds such as benzene, toluene, xylene and related compounds are well developed. Recommended standards of occupational exposure to many of these compounds have been promulgated by NIOSH(54,55). Benzene, toluene and xylene are chemicals for which OSHA also has prepared or is currently preparing toxicity standards(56).

7.5 CONTROL TECHNOLOGIES

Treatment of refinery and coal conversion waste streams by the technologies described in Chapter 6.0 should result in the removal of substantial portions of many of the hazardous constituents. For example, treatment of aqueous wastes with activated carbon should result in the removal of many of the organics including low molecular weight aromatics, organometallics and PAHs. Particulates containing PAHs, heavy metals and organometallic compounds would be expected to be partially or totally removed by use of standard particulate control devices such as electrostatic precipitators, fabric filters and venturi scrubbers. The fate of many of these hazardous constituents in waste treatment processes and the effectiveness of the conventional control technology for their removal in refinery and coal conversion

TABLE 7-6. SUMMARY OF TOXICOLOGICAL AND ENVIRONMENTAL DATA FOR SELECT AROMATIC COMPOUNDS ASSOCIATED WITH REFINERY AND/OR COAL CONVERSION WASTES(44,45)

Parameter*	Compound		
	Benzene	Toluene	Xylene (meta)
MEG Category	15	15	15
MEG Hazard Indicator	X	MH	MH
Toxic Dosage	Inhalation,human-LCLo,20,000 ppm/5 min. Oral,rat-LD50,3800 mg/kg Intraperitoneal,rat-LDLo,1150 mg/kg Skin,mouse-LDLo,1200 g/kg Oral,dog-LDLo,2000 mg/kg Subcutaneous,frog-LDLo,1500 mg/kg Aquatic toxicity, TLm96:100-10 ppm	Inhalation,human-TCLo,200 ppm Oral,rat-TCLo,100 ppm Inhalation,rat-LCLo,5000 ppm/4 hr. Intraperitoneal,rat-LCLo,800 mg/kg Subcutaneous,rat-LDLo,5000 mg/kg Skin,rabbit-LD50,14 gm/kg Aquatic toxicity,TLm96:100-10 ppm	Oral,rat-LD50,5000 mg/kg Inhalation,rat-LCLo,8000 ppm/4 hr. Intraperitoneal,rat-LDLo,2000 mg/kg Subcutaneous,rat-LDLo,5000 mg/kg
Toxicology	• Poisoning commonly occurs through inhalation of vapor and skin absorption. • Chronic poisoning systoms include fatigue, headache, dizziness, nausea; later, pallor, nosebleeds, and purpura may develop. • Acute poisoning symptoms include coma and death. • Chronic rather than acute poisoning is most common in industry.	--	--
Carcinogenicity	Yes (suspected)	No	No
Toxic Hazard Rating			
Acute Local	Irritant - 2; Ingestion - 1; Inhalation Inhalation - 1	Irritant - 1	Irritant - 1
Acute Systemic	Ingestion - 2; Inhalation - 2; Skin Absorption - 2	Ingestion - 2; Inhalation - 2; Skin Absorption - 1	Inhalation - 2; Skin Absorption - 2
Chronic Local	0	Irritant - 1	Irritant - 1
Chronic Systemic	Ingestion - 3; Inhalation - 3; Skin Absorption - 3	Ingestion - 2; Inhalation - 2; Skin Absorption - 2	Inhalation - 2; Skin Absorption - 2
Fire Hazard	Dangerous; can react vigorously with oxidizing materials	Dangerous	Dangerous
Explosion Hazard	Moderate	Moderate	Moderate
Disaster Hazard	Dangerous; highly flammable	Moderate dangerous; can react vigorously with oxidizing materials.	Dangerous, flammable Dangerous; flammable
Standards and Regulations			
OSHA			
Air, TWA	10 ppm	200 ppm	--
Air, ceiling conc.	25 ppm	300 ppm	--
Air, peak conc.	50 ppm/10 min	500/10 min.	--
Criteria Documents			
Air, TWA	--	100 ppm	--
Air, ceiling conc.	--	200/10 min.	--

(continued)

TABLE 7-6. CONTINUED

Parameter*	Compound			
	Aniline	Naphthylamine (-)	4-dimethyl Aminoazobenzene	Naphthalene
MEG Category	10C	10C	10C	21
MEG Hazard Indicator	NH	X	--	--
Toxic Dosage	Oral,human-LDLo,350 mg/kg Oral,rat-LD50,400 mg/kg Inhalation,rat-LCLo,250 ppm/4 hr. Subcutaneous,mouse-LDLo,480 mg/kg Oral,cat-LDLo,1750 mg/kg Skin,rabbit-LD50,820 mg/kg Aquatic toxicity, TLm96:100-10 ppm	Oral,rat-LD50,779 mg/kg Subcutaneous,mouse-TDLo,25 mg/kg Subcutaneous,rabbit-LDLo,300 mg/kg Oral,mammalian-LDLo,4000 mg/kg	Oral,rat-LD50,200 mg/kg Skin,rat-TDLo,155 mg/kg Intraperitoneal,rat-LD50,500 mg/kg Oral,mouse-TDLo,11g/kg Oral,dog,TDLo,9740 mg/kg	Oral,human-LDLo,100 mg/kg Oral,rat-LD50,1930 mg/kg Subcutaneous,rat-TDLo,3500 mg/kg/93 days Intraperitneal,mouse-LDLo,150 mg/kg Aquatic toxicity,TLm96:10-1 ppm
Toxicology	• Acute exposure results in formation of methemoglobin, with resulting anoxemia and depression of central nervous system. • In less acute exposures, there may be hemolysis of red blood cells, followed by stimulation of the bone marrow and attempts at regeneration.	• Suspected as cause of urinary bladder cancer.	• Causes liver cancer on an acute basis in rats and mice.	• Systemic reactions include nausea, headache, fever, anemia, liver damage, convulsions and coma.
Carcinogenicity	Suspected	Yes	Yes	No
Toxic Hazard Rating				
Acute Local	Allergen - 2	Irritant - 2	--	Irritant - 2
Acute Systemic	Ingestion - 3; Inhalation - 3; Skin Absorption - 3	Ingestion - 3; Inhalation - 3; Skin Absorption - 3	--	Ingestion - 2; Inhalation - 2; Skin Absorption - 2
Chronic Local	Allergen - 2	U	--	Irritant - 1
Chronic Systemic	Ingestion - 3; Inhalation - 3; Skin Absorption - 3	Ingestion - 3; Inhalation - 3; Skin Absorption - 3	--	Ingestion - 2; Inhalation - 1; Skin Absorption - 2
Fire Hazard	Moderate	Slight	--	Moderate
Explosion Hazard	--	--	--	--
Disaster Hazard	Dangerous	--	--	Moderate
Standards and Regulations				
OSHA				
Air, TWA	5 ppm-(skin)	--	--	- 10 ppm
Air, ceiling conc.	--	--	--	--
Air, peak conc.	--	--	--	--
Criteria Documents				
Air, TWA	--	--	--	--
Air, ceiling conc.	--	--	--	--
			U.S. Occupational Health Standard: carcinogen	

*For definition of terms and ratings, see Table 7-2.

application have not been studied. Accordingly, the need for additional control processes cannot be defined at this time.

Within a refinery or a coal conversion plant measures should be instituted to minimize worker exposure to hazardous chemicals. Such worker exposure control measures would be an element of the overall industrial hygiene program for the plant. Such programs are in effect in all U.S. refineries and similar programs would most likely be utilized in coal conversion plants. The following are examples of in-plant measures which would reduce worker exposure to hazardous chemicals:

- Elimination of spills and leaks through routine monitoring and maintenance and use of proper cleanup procedures in the event of accidental spillage
- Minimization of dermal contact with raw materials, intermediate products, and by-products through use of closed systems (where possible), proper ventilation and protective clothing.
- Use of documentation systems for industrial hygiene data and accidents.

Detailed recommendations and practices for industrial control of hazardous substances are presented in numerous documents and manuals published by NIOSH (e.g., Reference 44).

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